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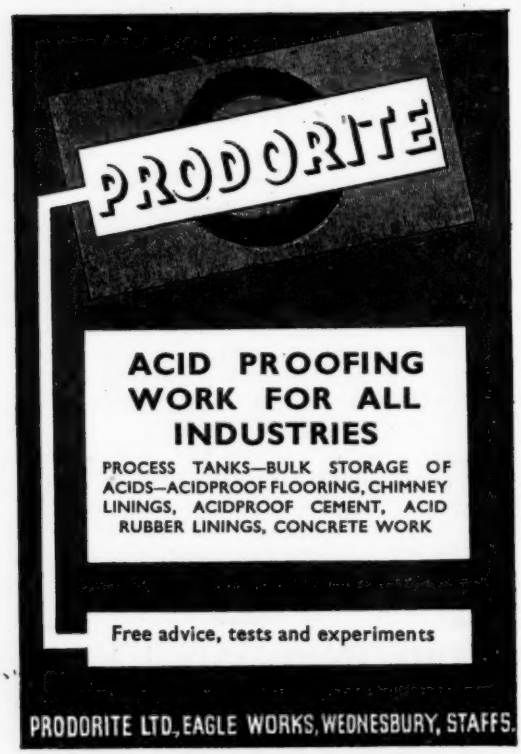
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The Gravimetric Micro-Determination of Magnesium. By P. F. HOLT.

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85. *Erucic Acid. Preparation of Erucic Acid. General Oxidation Reactions. Oxidation with Gaseous Oxygen.*

By Charles Dorée and Albert C. Pepper.

A method for the preparation of erucic acid, m. p. 33·8°, iodine value 75, from rape seed oil, in yields of 25—30%, is described.

Hydrogen peroxide, without a catalyst, converts erucic acid into 13 : 14-dihydroxybehenic acid, m. p. 101°, and brassidic acid into the isomer, m. p. 132°, but if osmium tetroxide is present erucic acid gives the derivative of m. p. 132° and brassidic acid that of m. p. 101°.

The allocation of the "*cis*"*-relationship to the 13 : 14-dihydroxybehenic acid, m. p. 101°, is supported by measurement of the rates of reaction of the isomers with lead tetra-acetate.

Neutral potassium permanganate with potassium erucate gives 13 : 14-dihydroxybehenic acid, m. p. 132°, and a mixture of isomeric hydroxy-ketobehenic acids. Perbenzoic acid gives oxidoerucic acid, which on hydrolysis yields 13 : 14-dihydroxybehenic acid, m. p. 101°, whereas oxidobrassidic acid yields the isomeric acid, m. p. 132°. Periodic acid, like lead tetra-acetate, converts the 13 : 14-dihydroxybehenic acids into nonaldehyde and brassylic semialdehyde.

Methyl erucate and brassidate are converted by hydrogen peroxide into *methyl dihydroxybehenates*, which give the 13 : 14-dihydroxybehenic acids, m. p. 101° and m. p. 132°, respectively. *Methyl oxidoerucate*, m. p. 28°, and *methyl oxidobrassidate*, m. p. 42·3°, are formed by the action of perbenzoic acid on the respective esters.

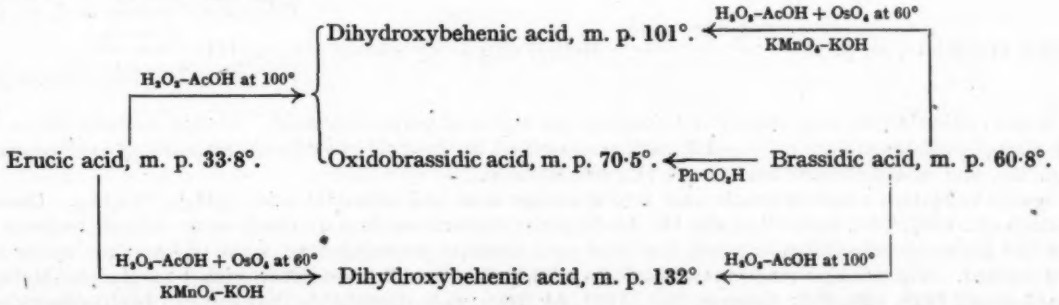
When treated with oxygen at 70° in the presence of a catalyst, erucic acid gives oxidoerucic acid, but at 120°, or at 70° in acetic anhydride solution, oxidobrassidic acid is formed. No free dihydroxy-acids are present, but if the residue is saponified, 13 : 14-dihydroxybehenic acid, m. p. 132°, is obtained in each case. Methyl erucate, treated at 70° with the addition of cobalt erucate, gives methyl oxidobrassidate and a complex which, after saponification, gives 13 : 14-dihydroxybehenic acid, m. p. 132°.

By the methods previously described for the preparation of erucic acid from rape seed oil, the pure acid has never been obtained in satisfactory quantity. The lead and lithium salting process, successfully used by Hilditch (*J. Soc. Chem. Ind.*, 1925, **44**, 43T) with the fatty acids of olive oil, gave less than 20% of erucic acid of low iodine value. The fractionation of the methyl esters (Grün and Janko, *A.*, 1916, i, 789; Holde and Wilke, *A.*, 1922, i, 713), followed by fractional precipitation of the acids obtained with lithium acetate, gave no more than 5% of pure erucic acid, iodine value 75. Direct crystallisation of the mixed fatty acids from alcohol (Reimer and Will, *Ber.*, 1886, **19**, 3320; Noller and Talbot, *Organic Syntheses*, 1930, **10**, 44) gave, however, a crude acid, m. p. 33·3°, iodine value 73, in good yields (30—35%), but fractional distillation of the mixed acids (Caldwell and Dye, *Ind. Eng. Chem.*, 1933, **25**, 338; Lepkovsky, Feskov, and Evans, *J. Amer. Chem. Soc.*, 1936, **58**, 978), stated to yield 40% of erucic acid, gave only 8% of a product of iodine value 72.

Starting from the crude product obtained by the method of Noller and Talbot (*loc. cit.*), we were unable to raise the iodine value above 73·5 by crystallisation from solvents or by distillation in a vacuum either of the mixed acids or of their methyl esters. By the addition of a lead salt to the alcoholic solution in fractions of the total required for complete precipitation (Täufel and Bauschinger, *Z. angew. Chem.*, 1928, **41**, 157) a satisfactory purification was, however, effected and erucic acid, m. p. 33·8°, iodine value 75, was readily obtained in yields of 25% upwards, calculated on the original rape seed oil.

The general and gaseous oxidation of oleic acid has been investigated by a number of workers. Primary products are oxido-oleic acid, the 9 : 10-dihydroxystearic acids, m. p. 95° and 132°, and the 9-hydroxy-10-keto- and 10-hydroxy-9-keto-stearic acids respectively. The *trans*-isomer, elaidic acid, gives similar products, but a reagent which produces one of the dihydroxystearic acids from oleic acid always produces the isomeric form from elaidic acid.

Erucic acid, $C_{22}H_{42}O_2$, Δ^{13} (*cis*), and brassidic acid (*trans*) form a similar pair of isomeric fatty acids. Their general behaviour on oxidation has now been investigated and some of the experimental results are summarised in the following scheme:



Hydrogen peroxide in boiling acetone had no action on erucic or brassidic acid, but in glacial acetic acid at 100° oxidation took place, giving in the absence of a catalyst, 13 : 14-dihydroxybehenic acid, m. p. 101°, and

* The terms "*cis*" and "*trans*" applied to these acids are used in accordance with the practice of previous writers (cf. Marsden and Rideal, J., 1928, 1169).

in the presence of osmium tetroxide the isomer, m. p. 132°. The converse is observed with brassidic acid. Oleic and elaidic acids behave similarly in the absence of a catalyst, 9 : 10-dihydroxystearic acids, m. p. 95° and 132°, respectively being formed (Hilditch, J., 1926, 1828). In the presence of osmium tetroxide, we find that oleic acid gives the acid of m. p. 132° and elaidic acid that of m. p. 95°. An inversion apparently due to the catalyst takes place and it is worthy of note that when vanadium pentoxide was substituted for osmium tetroxide, hydrogen peroxide was without action. The oxidative effect of hydrogen peroxide with osmium tetroxide as catalyst resembles that of alkaline permanganate in that only one of the isomeric dihydroxy-acids is formed in each case.

After removal of the dihydroxybehenic acid from the non-catalytic oxidation product of erucic acid, an oil was left which, on distillation, gave some 30% of its weight of a solid, b. p. 220—240°/3 mm., from which oxidobrassidic acid was isolated. The general reactions of the oil indicated that it might consist of a mixture of erucic acid peroxide and of acetylated derivatives of hydroxy-acids which decomposed on distillation, oxidobrassidic acid being one of the products.

Earlier results showing that alkaline potassium permanganate converted erucic acid exclusively into the 13 : 14-dihydroxybehenic acid, m. p. 132°, and brassidic acid into that of m. p. 101° have been confirmed. With the modified technique of Lapworth and Mottram (J., 1925, **127**, 1628) yields of 80—90% of the dihydroxy-acids were obtained.

Neutral potassium permanganate, however, acting on potassium erucate under controlled conditions (King, J., 1936, 1789), gave in addition to dihydroxybehenic acid, m. p. 132°, a mixture of the two hydroxyketobehenic acids, which were isolated as semicarbazones.

The oxido-derivatives of erucic and brassidic acids are probably primary products of oxidation. Albitski (*J. pr. Chem.*, 1900, **61**, 65) attempted to prepare them from the chlorohydrins, but could not isolate definite products. Warmbrunn and Stutzer (*Ber.*, 1903, **36**, 3604), through bromohydroxybehenic acid, $C_{22}H_{43}O_3Br$, obtained an oxidoerucic acid, m. p. 64°. Brassidic acid similarly gave an oxido-acid, m. p. 71°, which was very stable. It required heating with aqueous potassium hydroxide at 170° to give dihydroxybehenic acid, m. p. 132°.

Bauer and Bähr (*J. pr. Chem.*, 1929, **122**, 201) had obtained an oxidoerucic acid, m. p. 67·5°, by the action of perbenzoic acid on erucic acid, which after alkaline hydrolysis at 170° gave the higher-melting (132°) dihydroxybehenic acid. If this is correct, erucic acid (*cis*) through the oxido-acid gives rise to the "*trans*"-dihydroxy-acid, whereas oleic acid (*cis*) through oxido-oleic acid yields the "*cis*"-dihydroxy-acid. We now find that the oxido-derivatives of erucic and brassidic acids are readily obtained by the use of perbenzoic acid. Their properties and reactions are shown below, erucic acid (*cis*) giving rise to the "*cis*"-dihydroxy-derivative :

$$\text{Erucic acid} \xrightarrow{\text{Ph·CO}_3\text{H}} \text{Oxidoerucic acid, m. p. 63·5°} \xrightarrow{\text{hydrolysis}} \text{Dihydroxybehenic acid, m. p. 101°}$$

$$\text{Brassidic acid} \xrightarrow{\text{Ph·CO}_3\text{H}} \text{Oxidobrassidic acid, m. p. 70·5°} \xrightarrow{\text{hydrolysis}} \text{Dihydroxybehenic acid, m. p. 132°}$$

The oxido-acids were difficult to hydrolyse in alkaline solution, but aqueous-alcoholic hydrochloric acid was effective. The oxidoerucic acid of Bauer and Bähr (*loc. cit.*) was impure and the severe hydrolytic treatment probably brought about inversion.

The chlorohydrin synthesis was repeated in the case of erucic acid, but the yield of oxido-acid (about 10%) compared unfavourably with the 60—70% obtained by the use of perbenzoic acid.

A similar series of experiments was carried out on methyl erucate and brassidate. Their reactions with hydrogen peroxide are shown below, the dihydroxy-acid derived from each ester being the same as that obtained directly from the acid :

$$\text{Methyl erucate, b. p. 183°/0·2 mm.} \xrightarrow{H_2O_2\text{–AcOH at 100°}} \text{Methyl dihydroxybehenate, m. p. 78°} \xrightarrow{\text{hydrolysis}} \text{Dihydroxybehenic acid, m. p. 101°}$$

$$\text{Methyl brassidate, m. p. 33°} \xrightarrow{H_2O_2\text{–AcOH at 100°}} \text{Methyl dihydroxybehenate, m. p. 111°} \xrightarrow{\text{hydrolysis}} \text{Dihydroxybehenic acid, m. p. 133°}$$

Methyl oxido-esters were readily obtained by the action of perbenzoic acid. *Methyl oxidoerucate*, m. p. 28°, and *methyl oxidobrassidate*, m. p. 42·3°, when saponified in the cold gave the corresponding oxidoerucic acid, m. p. 63°, and oxidobrassidic acid, m. p. 71°, respectively.

Severe oxidation resolves erucic acid into *n*-nonoic acid and brassylic acid, $[CH_2]_{11}(CO_2H)_2$. Green and Hilditch (J., 1937, 764) found that the 13 : 14-dihydroxybehenic acids were much more difficult to break down than the 9 : 10-dihydroxystearic acids, but that with alkaline permanganate, acids of lower molecular weight were formed. The specific reactions of periodic acid and of lead tetra-acetate with 1 : 2-glycols (Malaprade, *Compt. rend.*, 1928, **186**, 382; Criegee, *Ber.*, 1931, **64**, 260) made it probable that the 13 : 14-dihydroxybehenic acids would be smoothly resolved by these reagents. This proved to be the case. Potassium periodate gave nonaldehyde in quantitative yield together with brassylic semialdehyde, which was isolated from a polymerised product initially formed (cf. King, J., 1938, 1826). Lead tetra-acetate also reacts smoothly with *cis*-1 : 2-glycols, whereas *trans*-1 : 2-glycols are less readily attacked. Both 13 : 14-dihydroxybehenic

acids were oxidised by this reagent, giving in each case nonaldehyde and *brassylic semialdehyde*. Comparative oxidation at 40° following the procedure of Criegee (*Ber.*, 1932, **65**, 1770) gave the following results:

Mols. of $Pb(OAc)_4$ consumed per 1 mol. of dihydroxy-acid.

Time (mins.)	5	20	50	80
Acid, m.p. 101°	0·778	0·996	1·370	1·660
Acid, m.p. 132°	0·751	0·890	0·929	0·960

These figures support the opinion that the acid, m. p. 101°, has the "*cis*"-configuration (cf. Hilditch and Jasperson, *Nature*, 1941, **147**, 327).

The action of oxygen on erucic acid does not appear to have been investigated. Skellon (*J. Soc. Chem. Ind.*, 1931, **50**, 382T) found that its action on oleic acid at 120° produced *iso*oleic acid, 9 : 10-dihydroxystearic acid, m. p. 132°, and nonoic acid. With a cobalt catalyst present, azelaic acid, 10-hydroxystearic acid, m. p. 84°, and the isomeric 9 : 10-dihydroxystearic acids, m. p. 95° and 132°, were obtained. Ellis (*Biochem. J.*, 1932, **26**, 791) studied the absorption of oxygen by oleic and elaidic acids when finely dispersed on filter-paper. At 65—75°, with a cobalt catalyst, oleic acid showed an oxygen uptake of 20% in 36 hours and later the same uptake was achieved in 7 hours (*ibid.*, 1936, **30**, 753).

Under such restrained conditions both oleic and elaidic acids gave oxidoelaidic acid, so an oxido-derivative would appear to be an initial product of oxidation. The difference in the results obtained by these authors is probably due to the fact that the former saponified the oxidised material prior to separating its constituents, whereas the latter did not. The action of alkali would hydrolyse the oxido-acid and induce reactions of condensation and polymerisation.

The apparatus employed by us for the gaseous oxidation of erucic acid consisted of a large, electrically heated oil-bath fitted with thermostatic temperature control and a slowly moving stirrer. Purified dry oxygen was passed through a meter into the melted acid, which was contained in large Pyrex test-tubes set in the bath in parallel. The oxygen inlet tubes ended in a bubbler device which produced a fine stream of bubbles, bringing the gas into uniform contact with the liquid under treatment. Volatile products were collected in a cooled trap-bottle, and carbon dioxide absorbed in baryta solution.

Oxidations were carried out at 70° and 120° with and without the addition of cobalt erucate (0·6%). About 25 g. of acid were used in each experiment with an oxygen flow of 5 l. per hour. To ascertain the rate of action under these conditions, samples were withdrawn at intervals, and the constants of the product determined. Typical results for erucic acid at 120° are shown below:

Time in hours	0		4·5		7·8		12·0	
Iodine value	(*a*) 75	(*b*) 75	(*a*) 59	(*b*) 57	(*a*) 48	(*b*) 43·5	(*a*) 37	(*b*) 34·5
Acid value	(*a*) 166	(*b*) 166	(*a*) 150	(*b*) 148	(*a*) 144	(*b*) 142	(*a*) 142	(*b*) 139

(*a*) with and (*b*) without the addition of cobalt erucate.

The iodine value is reduced to about one half in 12 hours at 120° whether a catalyst is present or not; the acid value falls at a much slower rate. When the acid was heated for 12 hours at 120° without oxygen, no change in its constants could be observed. At 70° the rate of oxidation was slower, the iodine value falling to 53 in 12 hours and to 38 in 24 hours, the acid value increasing slightly during that period. The end products were much less coloured at 70° than at 120°.

The resolution of the oxidised material was effected through the observation that oxido-erucic and -brassidic acids crystallised readily from 95% alcohol, whereas the complex oxidation products remained soluble even at 0°. Further separation of the alcohol-soluble fraction was obtained by extraction of the residue with light petroleum. The following is a typical result obtained with the oxidation product of erucic acid formed at 120° in the presence of cobalt erucate.

Product.	Yield, %.
(*a*) Oxidobrassidic acid	12
(*b*) Light petroleum-soluble, giving after saponification 10% of its weight of dihydroxybehenic acid, m. p. 132°	40
(*c*)) Brown residue insoluble in light petroleum, giving on saponification 11% of dihydroxybehenic acid, m. p. 132°	39

No brassylic acid could be obtained from fraction (*b*) and neither fraction (*b*) nor (*c*) gave dihydroxybehenic acid prior to saponification. An attempt to isolate ketol-behenic acids from fraction (*c*) by conversion into the semicarbazones and separation in ethylene dichloride solution was unsuccessful. A product obtained at 120° in the absence of a catalyst gave only 1% of oxidobrassidic acid. From the fractions soluble and insoluble in light petroleum neither brassylic nor dihydroxybehenic acid could be isolated, but after saponification a total yield of 12% of 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained.

The course of oxidation at 70° was somewhat different. Ellis (*Biochem. J.*, 1936, **30**, 753) had shown that both oleic and elaidic acids, when treated with oxygen at this temperature, gave oxidoelaidic acid, oxido-oleic acid not being formed in appreciable quantity. It was expected that the catalytic gaseous oxidation of erucic acid at 70° would yield oxidobrassidic acid, but instead oxidoerucic acid was obtained, the yield being about 15% (24 hours) and 20% (50 hours).

A typical oxidation of erucic acid (24 hours) with 0·6% of cobalt erucate at 70° gave the following results:

Product.	Yield, %.
(*a*) Oxidoerucic acid, m. p. 63·5°	15
(*b*) Light petroleum-soluble, giving after saponification 6% of its weight of dihydroxybehenic acid, m. p. 132°	48
(*c*) Residue insoluble in light petroleum, giving after saponification 17% of its weight of dihydroxybehenic acid, m. p. 132°	32

Fraction (*b*) gave on distillation in a vacuum a small amount of nonoic acid and from fraction (*c*) by extraction with 50% alcohol a little brassylic acid, m. p. 111°, was obtained. No brassylic semialdehyde could be isolated from fraction (*c*) after boiling with dilute sulphuric acid, a method by which this substance was obtained from the product of oxidation of erucic acid with potassium periodate.

The oxidation of oleic and erucic acids with hydrogen peroxide proceeds most readily in the presence of acetic acid. This was attributed by Böeseken (*Rec. Trav. chim.*, 1926, **45**, 842; 1927, **46**, 622) to the presence of peracetic acid. An experiment was therefore carried out on the catalytic gaseous oxidation of erucic acid dissolved in twice its weight of acetic anhydride at 70°. The reaction was rapid, the iodine value falling to 38 (6 hours), 20 (12 hours) and 16 (after 15 hours), a white solid forming in the tube. This proved, however, to be oxidobrassidic acid (15%) and from the solution a small amount only of dihydroxybehenic acid, m. p. 132°, was obtained. The presence of acetic anhydride therefore brings about the formation of oxidobrassidic acid and its normal hydrolysis product, dihydroxybehenic acid, m. p. 132°, whereas in its absence oxidoerucic acid is the main product of reaction at 70°.

Methyl erucate, when treated with oxygen at 70° in the absence of a catalyst, was hardly affected even after 24 hours. In the presence of cobalt erucate reaction was immediate, the iodine value of 72 becoming 60 (3 hours), 38 (12 hours) and 21·5 (after 24 hours), the acid value increasing slowly from 0 to 50. The free acids were extracted with potassium carbonate solution and from the neutral residue methyl oxidobrassidate was obtained. The following represents a typical analysis:

Product.	Yield, %.
(*a*) Free oxidised fatty acids	18
(*b*) Neutral oxidised ester fraction consisting of	
(i) methyl oxidobrassidate	14·5
(ii) a complex which after saponification gave 12% of dihydroxybehenic acid, m. p. 132°	48·5

An oxidation of methyl erucate in the presence of acetic anhydride and cobalt erucate at 70° gave a similar result. The iodine value fell to 21·9 in 12 hours and methyl oxidobrassidate was the main product.

An oxidation at 120° in the presence of cobalt erucate gave the following:

Product.	Yield, %.
(*a*) Free oxidised acids	15
(*b*) Neutral oxidised ester fraction consisting of	
(i) methyl oxidobrassidate	9
(ii) a complex which after saponification gave 10% of its weight of dihydroxybehenic acid, m. p. 132°	74

No other definite products could be obtained.

The gaseous oxidation of erucic acid therefore leads generally to the formation of an oxido-derivative of the *trans*-isomer, brassidic acid. The reaction is thus similar to that observed in the gaseous oxidation of oleic acid where oxidoelaidic acid (*trans*) is the main product, oxido-oleic acid not being formed (Ellis, *loc. cit.*).

Erucic acid, however, at 70°, exceptionally, gives oxidoerucic acid, the lower temperature apparently preventing inversion, although methyl erucate, at the same temperature, forms the oxidobrassidic acid derivative.

Both oxido-acids are resistant to hydrolysis, which may account for the absence of dihydroxy-acids in the original oxidation product. After saponification of the complex, however, 13 : 14-dihydroxybehenic acid, m. p. 132°—the normal hydrolysis product of oxidobrassidic acid—is always formed in considerable quantity. Scission products of lower molecular weight were practically absent.

Unstable peroxides may also be among the initial products of oxygen uptake. From them aldehydic compounds could be formed which, either by reaction with other substances present, or by polymerisation, give rise to the resistant brown residue observed in all these oxidations.

Experimental.

Preparation of Erucic Acid.—800 G. of rape seed oil in 1 l. of 95% alcohol were heated for 6 hours with 200 g. of potassium hydroxide in 100 ml. of water. The alcohol was removed by distillation, the potassium salts treated with about 1·5 l. of water, and the syrup acidified with 10% hydrochloric acid and boiled. After cooling, the cake of fatty acids was washed and dried (yield, 700 g.). To remove liquid fatty acid impurities, the cake (700 g.) was dissolved in 2 l. of warm alcohol and cooled in ice with stirring. As soon as crystals formed, the solution was filtered, and the filtrate left for 1 day in the ice-chest. The erucic acid deposited was removed, and a second crop obtained after 1 more day. These crops were recrystallised several times from alcohol, giving 250 g. of erucic acid, m. p. 33·3°, I.V. 72·4. To remove solid fatty acids, the 250 g. of crude acid in 1·5 l. of 95% alcohol were treated with a solution containing 6 g. of lead acetate dissolved in the minimum quantity of water and made up to 1·5 l. with alcohol, both

solutions being kept at 75°. After 12 hours at 20° the solid was removed; the filtrate, after 1 day at 0°, deposited an acid which, after several crystallisations from 500 ml. portions of absolute alcohol, gave 215 g. or 28% of erucic acid, m. p. 33·8°, I.V. 75·0, A.V. 166.

Preparation of Brassidic Acid.—(*a*) 10 G. of erucic acid, suspended in 250 ml. of an aqueous solution containing 75 ml. of nitric acid (*d* 1·42), were warmed to 50°, and 2 g. of finely powdered sodium nitrite gradually added. The fatty acid layer solidified and was remelted by warming at 70° for 15 minutes. After cooling, the solid was washed and crystallised several times from alcohol, giving brassidic acid, m. p. 60·8°, I.V. 73·8 (yield, 70%). (*b*) A mixture of 20 g. of erucic acid and 2 g. of powdered selenium was heated for 3 hours at 200—210°. The brown mass was extracted with 5% potassium hydroxide solution, the extract filtered and acidified, and the fatty acids removed in ether. The crude product was crystallised as before, leaving 8·5 g. or 42·5% of brassidic acid, m. p. 60·5°, I.V. 74.

Oxidation of Erucic Acid with Hydrogen Peroxide.—(a) *In acetone solution.* Erucic acid (2 g.) in 100 ml. of acetone with 20 ml. of hydrogen peroxide (100 vol.) was refluxed for 8 hours. After removal of the solvent, unchanged erucic acid (1·9 g.) was left. Heating for 50 hours gave the same result. Brassidic acid similarly was not oxidised.

(b) *In glacial acetic acid solution.* To 50 g. of erucic acid in 250 ml. of glacial acetic acid, 100 ml. of hydrogen peroxide (100 vol.) were added gradually during 2 hours at 100°. Refluxing was continued for a further 2 hours. An oily layer separated which gradually dissolved. The solution was poured into water, and the precipitate washed and crystallised from absolute alcohol, giving dihydroxybehenic acid (32 g.), m. p. 101°, I.V. 0 (Found: C, 70·9; H, 10·6. Calc. for $C_{22}H_{44}O_4$: C, 70·9; H, 11·8%). The m. p. was not depressed by the acid prepared by oxidation of brassidic acid with alkaline permanganate.

The alcoholic mother-liquors gave a pale yellow oil which liberated iodine from potassium iodide equivalent to 22·2% of erucic acid peroxide. About 33% distilled at 220—240°/3 mm., forming a white solid which, when crystallised from alcohol, gave oxidobrassidic acid, m. p. 69·5°, unchanged in admixture with a specimen made by the action of perbenzoic acid on brassidic acid.

Brassidic acid, when treated similarly (5 g. in 30 ml. of glacial acetic acid with 15 ml. of hydrogen peroxide; heating for 4—6 hours), gave dihydroxybehenic acid, m. p. 132°.

(c) *In glacial acetic acid solution with vanadium pentoxide.* 2 G. of erucic or brassidic acid in 25 ml. of acetic acid containing 0·1 g. of vanadium pentoxide, after treatment with 10 ml. of hydrogen peroxide for 10 days at room temperature or 40 hours at 70°, were recovered unchanged.

(d) *In glacial acetic acid solution with osmium tetroxide.* To 5 g. of erucic acid in 50 ml. of acetic acid containing 0·1 g. of osmium tetroxide, were added gradually 10 ml. of hydrogen peroxide. After 50 days at room temperature the solvent was removed, and the black residue extracted with alcohol. Traces of catalyst were removed by the addition of 20% of water and rapid filtration. After cooling in the ice chest and recrystallisation from alcohol, white crystals of dihydroxybehenic acid, m. p. 130°, I.V. 0, A.V. 151, were obtained. The m. p. was not depressed by an authentic specimen.

If, after the addition of hydrogen peroxide, the temperature was raised to 60° and maintained for 1 hour, the same result was obtained. Dihydroxybehenic acid, m. p. 131°, was formed; yield, 65% (Found: C, 70·8; H, 12·0. Calc.: C, 70·9; H, 11·8%).

Brassidic acid (2·5 g.), in 50 ml. of glacial acetic acid containing 0·1 g. of osmium tetroxide, was treated with 10 ml. of hydrogen peroxide at 30° and heated at 60° for 1 hour. After cooling in the ice-chest the solid was removed and after crystallisation from alcohol gave dihydroxybehenic acid, m. p. 100·3°, not depressed by an authentic specimen.

Oxidation of Oleic and Elaidic Acids with Hydrogen Peroxide in Acetic Acid Solution with Osmium Tetroxide.—2·5 G. of oleic acid were dissolved in 50 ml. of glacial acetic acid, cooled to room temperature, and 0·1 g. of osmium tetroxide added, followed by 10 ml. of hydrogen peroxide (100 vol.). The mixture was warmed at 60° for ½ hour and cooled in the ice-chest overnight, the liquid filtered, and the residue washed with water and crystallised from alcohol. Dihydroxystearic acid, m. p. 131·2°, was obtained; yield, 60%.

Elaidic acid, treated similarly, gave dihydroxystearic acid, m. p. 95°, identical with that obtained by the action of hydrogen peroxide on oleic acid in glacial acetic acid solution alone.

Oxidation with Alkaline Potassium Permanganate.—2 G. of erucic acid in 5 ml. of absolute alcohol were treated with 4 g. of potassium hydroxide in 4 ml. of water. The alcohol was removed, and a solution of the residue in about 600 ml. of water was heated to 27°, 3 g. of potassium permanganate in 300 ml. of water rapidly added, and the whole maintained at 27° for 30 mins. with stirring. After treatment with sodium sulphite and excess of 20% hydrochloric acid, the solids were washed and crystallised from alcohol, giving 13 : 14-dihydroxybehenic acid, m. p. 132°. Yield, 85%.

Brassidic acid, treated in the same way, gave 13 : 14-dihydroxybehenic acid, m. p. 100·5°. Yield, 80%.

Oxidation of Potassium Erucate with Potassium Permanganate in Neutral Solution.—10 G. of erucic acid in the minimum quantity of alcohol were neutralised with N/2-alcoholic potassium hydroxide. The alcohol was removed, and the residue dissolved by adding water up to 1 l. and then diluted with hot water to 8 l. The solution was cooled to 40° (below which no reaction took place) and 9·8 g. of potassium permanganate in 1·5 l. of water, also at 40°, were run in with stirring, which was continued for 15 minutes. A solution of 32 g. of sodium sulphite in 300 ml. of water was added, followed by excess of dilute hydrochloric acid. The solid residue was washed and dried. It was extracted repeatedly with chloroform in small portions (total 150 ml.), the filtrate cooled in ice, and the crystals of dihydroxybehenic acid, m. p. 132°, removed. A small final crop was obtained on standing.

The chloroform was removed in a vacuum and the residue, while warm, was extracted with 400 ml. of light petroleum (b. p. 40—60°). After 24 hours at 0° a mixture of hydroxy-ketobehenic acids was deposited. A solution of this in 10 parts of chloroform was cooled to 0° and filtered, and the solvent removed in a vacuum. The residue, crystallised repeatedly from alcohol and acetone, gave crystals, m. p. 77°, setting point 73° (Found: C, 71·5; H, 11·5. *Hydroxyketobehenic acid*, $C_{22}H_{42}O_4$, requires C, 71·4; H, 11·4%).

The mixture of acids could not be separated by means of dilute alcohol, acetone or light petroleum. 2·4 G. of the mixed acids, m. p. 77°, in 4 ml. of alcohol were added to 2 g. of semicarbazide hydrochloride and 3 g. of sodium acetate dissolved in the minimum quantity of water (cf. King, J., 1936, 1789). The mixture was shaken, warmed to 60°, and kept. The solid was washed with ice-water, dried, and extracted with 20 ml. of boiling alcohol, and the solution left for 3 days at 0°. The semicarbazones obtained were purified further from absolute alcohol and dried, and 2 g. extracted with 50 ml. of ethylene dichloride at 60°. The filtrate, concentrated to 10 ml. and cooled, gave crystals, m. p. 134° after recrystallisation from 80% alcohol (Found: C, 63·8; H, 10·1. The *semicarbazone* of hydroxyketobehenic acid, $C_{23}H_{45}O_4N_3$, requires C, 64·6; H, 10·6%).

The residue insoluble in ethylene dichloride, when crystallised from 80% alcohol, gave crystals of the second semicarbazone, m. p. 157·5°. The acids were not isolated from these derivatives.

Oxidation of Erucic and Brassidic Acids with Perbenzoic Acid.—10 G. of erucic acid in 20 ml. of chloroform were mixed at 0° with 200 ml. of a solution of perbenzoic acid in chloroform containing 0·008 g. of active oxygen per ml. After 10 days at 0° and 1 day at room temperature the solvent was removed in a vacuum, and the residue extracted with hot water till free from benzoic acid. The oil obtained was dissolved in 8 times its weight of alcohol and cooled,

and the crystals of oxidoerucic acid (7·5 g.) separated. After purification the m. p. was 63·5°, I.V. 0, A.V. 157 (Found: C, 74·5; H, 12·3. Calc. for $C_{22}H_{42}O_3$: C, 74·6; H, 11·9%). On hydrolysis by boiling for some hours with a large volume of aqueous alcoholic hydrochloric acid a solid was obtained which, crystallised from alcohol, yielded 13 : 14-dihydroxybehenic acid, m. p. 100°, not depressed by an authentic specimen.

7 G. of brassidic acid were treated with perbenzoic acid as above. The oxidobrassidic acid obtained (4·1 g.) had m. p. 70°, I.V. 0, A.V. 159 (Found: C, 74·8; H, 12·0. Calc. for $C_{22}H_{42}O_3$: C, 74·6; H, 11·9%). On hydrolysis 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained.

Chlorohydrin Synthesis of Oxidoerucic Acid.—To a solution of 15 g. of erucic acid in 250 ml. of ether, 230 ml. of 5% sodium hypochlorite solution were added. Carbon dioxide was passed into the liquid to saturation, the ether being replaced from time to time. After 12 hours the ether was washed and distilled, and the residue dissolved in 200 ml. of absolute alcohol, cooled to 0°, and filtered. Excess of sodium ethoxide was added, and the mixture warmed to 50°, left overnight, acidified with 5% hydrochloric acid, and cooled. The solid obtained gave oxidoerucic acid, m. p. 63·2°, after crystallisation from alcohol. Yield, 10%.

Preparation of Methyl Erucate and Methyl Brassidate.—100 G. of erucic acid, 300 ml. of anhydrous methyl alcohol, and 3·5 g. of concentrated sulphuric acid were refluxed for 6 hours, the bulk of the alcohol removed in a vacuum, the residue poured into cold water, and the oil taken up in ether, washed with dilute sodium carbonate solution and with water, and distilled. The fraction, b. p. 182—184°/0·2 mm., was methyl erucate (80·5 g.), I.V. 71·2, A.V. 0.

Methyl brassidate, similarly prepared and purified finally from alcohol, had m. p. 33°, I.V. 70·1, A.V. 0. Yield, 75%.

Oxidation of Methyl Erucate and Methyl Brassidate with Hydrogen Peroxide.—20 G. of methyl erucate in 40 ml. of glacial acetic acid were treated with 35 ml. of hydrogen peroxide (100 vol.). The oily layer formed disappeared after heating on the water-bath for 2 hours and after a further 2 hours the solution was poured into 300 ml. of water. The solid deposited at 0°, crystallised from methyl alcohol, gave *methyl* 13 : 14-*dihydroxybehenate*, m. p. 78° (Found: C, 71·3; H, 11·8. $C_{23}H_{46}O_4$ requires C, 71·5; H, 11·9%). On saponification it gave 13 : 14-dihydroxybehenic acid, m. p. 100°.

Methyl brassidate, when oxidised similarly with hydrogen peroxide, gave *methyl* 13 : 14-*dihydroxybehenate*, m. p. 111°, in good yield (Found: C, 71·2; H, 11·7%). On saponification it gave 13 : 14-dihydroxybehenic acid, m. p. 131°.

Oxidation of Methyl Erucate and Methyl Brassidate with Perbenzoic Acid.—15 G. of methyl erucate in 100 ml. of chloroform were treated at 0° with 400 ml. of a cold chloroform solution containing perbenzoic acid equivalent to 0·006 g. of active oxygen per ml. After 10 days (ice-chest) the temperature was allowed to rise to 20°, and the chloroform removed (vacuum). The residue was extracted with hot water and dissolved in ether, the solution washed with sodium carbonate and dried, and the solvent removed. The oil left was crystallised from methyl alcohol, giving *methyl oxidoerucate* (12 g.), m. p. 28°, A.V. 2·0, I.V. 0 (Found: C, 74·8; H, 11·9. $C_{23}H_{44}O_3$ requires C, 75·0; H, 11·9%). Saponification with 0·5N-alcoholic potassium hydroxide for 1 day at room temperature gave oxidoerucic acid, m. p. 62·3°, not depressed by an authentic specimen.

Methyl brassidate, oxidised in the same way, gave *methyl oxidobrassidate*, m. p. 42·3°, A.V. 0, I.V. 0 (Found: C, 74·9; H, 11·8. $C_{23}H_{44}O_3$ requires C, 75·0; H, 11·9%). Saponification in the cold gave oxidobrassidic acid, m. p. 70·1°, unchanged in admixture with an authentic specimen.

Oxidation of Methyl 13 : 14-*Dihydroxybehenate with Lead Tetra-acetate.*—10 G. of the ester, m. p. 78°, in 120 ml. of glacial acetic acid were mixed with a solution of 33 g. of lead tetra-acetate in 250 ml. of hot glacial acetic acid. After 3 hours at 70° the mixture was poured into water. The product extracted by ether was dissolved in its own weight of light petroleum, washed, dried, and cooled to −10° for 1 day. The white solid obtained crystallised from 80% alcohol in plates, m. p. 51·8° (Found: C, 68·7; H, 10·1. *Methyl brassylate semialdehyde*, $C_{14}H_{26}O_3$, requires C, 69·4; H, 10·8%). As no aldehydic derivatives could be prepared, the identity of the product remains doubtful.

The filtrate from the light petroleum extract gave an oil which on distillation gave nonaldehyde, b. p. 50—52°/2·8 mm.; semicarbazone, m. p. 99·8°; 2 : 4-dinitrophenylhydrazone, m. p. 106°.

Oxidation of 13 : 14-*Dihydroxybehenic Acid, m. p.* 101°, *with Periodic Acid.*—16 G. of dihydroxybehenic acid in 400 ml. of 95% alcohol were mixed rapidly with a solution of 12 g. of potassium periodate in 600 ml. of N-sulphuric acid at 30°. After 15 mins. the cloudy solution was cooled and diluted with water. The product extracted by ether was distilled in steam. The distillate, extracted with ether, yielded an oil, one half of which, distilled (0·2 mm.), gave a main fraction, b. p. 51—53°, consisting of nonaldehyde (Found: C, 75·8; H, 12·7. Calc.: C, 76·0; H, 12·7%); semicarbazone, m. p. 99·5°; 2 : 4-dinitrophenylhydrazone, m. p. 106°.

The oil left after separation of the nonaldehyde rapidly darkened. The nonaldehyde was therefore removed from the second half of the original oil, and the residue at once cooled in ice. It was taken up in 95% alcohol and kept at 0°. Crystals (0·2 g.), m. p. 73°, separated; they gave no aldehydic reactions and were not further examined. The filtrate, after removal of the alcohol, left 3 g. of oil, which were heated for 30 mins. with 100 ml. of 8% sulphuric acid. The semi-solid material obtained was extracted with 50% alcohol and filtered hot. Crystalline plates, m. p. 87·5°, were obtained [Found: C, 68·0; H, 10·2; *M* (titration), 222. *Brassylic semialdehyde*, $C_{13}H_{24}O_3$, requires C, 68·4; H, 10·5%; *M*, 228]. The *semicarbazone* had m. p. 158·5° (Found: C, 59·2; H, 9·9. $C_{14}H_{27}O_3N_3$ requires C, 58·9; H, 9·5%). Oxidation gave brassylic acid, m. p. 111°, unchanged in admixture with an authentic specimen.

Oxidation of 13 : 14-*Dihydroxybehenic Acid, m. p.* 101°, *with Lead Tetra-acetate.*—20 G. of dihydroxybehenic acid in 250 ml. of glacial acetic acid were heated with 80 g. of lead tetra-acetate in 250 ml. of the same solvent at 70° for 3 hours, and the mixture poured into water. Ether extracted an oil, which on fractionation under low pressure gave a small quantity of acetic acid, followed by a mixture of acetic acid and nonaldehyde, b. p. up to 65°/8 mm., from which nonaldehyde (3·5 g.), b. p. 50—52°/2 mm., was separated. The residue in the flask which did not distil up to 130°/2 mm. weighed 8 g. It was dissolved in alcohol and, on cooling, gave 1·5 g. of fine crystals which after purification had m. p. 73°. This substance gave no aldehydic reactions. The alcoholic filtrate gave an oil which was heated with 200 ml. of 5% sulphuric acid for 30 mins. After cooling, the solid was removed, washed, and boiled out with 50% alcohol. The extract deposited crystalline plates which finally gave brassylic semialdehyde, m. p. 87·8° (Found: C, 68·8; H, 10·9%). The semicarbazone had m. p. 158°, unchanged in admixture with a sample prepared by the action of periodic acid on dihydroxybehenic acid. Oxidised with potassium permanganate, the aldehyde gave brassylic acid, m. p. 111°.

The oxidation of 13 : 14-dihydroxybehenic acid, m. p. 132°, with lead tetra-acetate gave the same scission products, nonaldehyde and brassylic semialdehyde.

The Rates of Reaction of the Two 13 : 14-*Dihydroxybehenic Acids with Lead Tetra-acetate.*—0·05 G. of the dihydroxy-acid in 20 ml. of glacial acetic acid was mixed with 10 ml. of 1·1N-lead tetra-acetate. The method of titration was that of Criegee (*loc. cit.*). The results are on p. 479.

General Method of Treatment with Oxygen.—Dry purified oxygen was passed at the rate of 5 l. per hour through the acid (25 g. units) in the apparatus described on p. 479. The catalyst, when used, was 0·6% of cobalt erucate in each case. The amount of carbon dioxide produced was small (1—2%).

Oxidation of erucic acid at 120° *in presence of a catalyst.* 20 G. of the product obtained after 12 hours' treatment with oxygen were dissolved in 100 g. of 95% alcohol and kept at 0° for 2 days. The white solid was removed and

crystallised several times from alcohol and acetone, giving oxidobrassidic acid, m. p. 70·5°. Yield, 12% (Found: C, 74·4; H, 12·1. Calc.: C, 74·6; H, 11·9%). On hydrolysis with aqueous alcoholic hydrochloric acid 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained.

The alcoholic filtrate was evaporated to dryness in a vacuum, and the residue (16 g.) dissolved in 100 ml. of light petroleum. On dilution with the solvent to 300 ml. a brown oil (8 g.) separated.

The solution in light petroleum might contain nonoic acid. It was kept at −20° for 8 hours, but no solid acid appeared. The solvent was removed, and the residue distilled in steam. Volatile acids were absent. Solution of the residue in alcohol and precipitation with lead acetate (20% of the total required) gave lead salts, which were extracted with hot alcohol. Lead nonoate would dissolve, but the acid could not be detected among the free acids obtained from the alcoholic extract. From the insoluble lead salts some erucic acid was obtained.

6 G. of the portion soluble in light petroleum were heated with alcoholic potassium hydroxide solution for 8 hours. The acids obtained on acidification were dissolved in 200 ml. of ether. The solution deposited a solid which, recrystallised from alcohol, left 0·6 g. (10%) of 13 : 14-dihydroxybehenic acid, m. p. 132°. This acid could not be detected in the brown oil (8 g.) insoluble in light petroleum, but after saponification of the oil as above 11% of 13 : 14-dihydroxybehenic acid was obtained.

A search for ketol-behenic acids was made by the method previously used for their isolation. The brown oil insoluble in light petroleum did not form a semicarbazone.

Oxidation of erucic acid at 120° *in the absence of a catalyst.* 17 G. of the product obtained after 12 hours' treatment were dissolved in 60 ml. of alcohol and kept below 0° for several days. The solid deposited gave oxidobrassidic acid, m. p. 70·5° (yield, 1%). The alcohol was removed, and the residue (16 g.) treated with light petroleum as before. The absence of nonoic acid and of dihydroxybehenic acid in the light petroleum-soluble portion (9 g.) was confirmed. After saponification for 8 hours as above, 8·5% of its weight of 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained. The light petroleum-insoluble fraction (8 g.) contained neither brassylic acid nor free dihydroxybehenic acid, but after saponification 16% of its weight of 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained.

Oxidation of erucic acid at 70° *in the presence of a catalyst.* 20 G. of the product obtained after 24 hours' treatment were dissolved in alcohol (100 ml.) and kept at 0° for 2 days. The solid deposited, after purification from alcohol and acetone and extraction with light petroleum, gave oxidoerucic acid, m. p. 63·7°, not depressed by a specimen prepared by the action of perbenzoic acid. Yield, 13·5% (Found: C, 74·3; H, 12·4. Calc.: C, 74·6; H, 11·9%). On hydrolysis 13 : 14-dihydroxybenenic acid, m. p. 100°, was formed.

The portion soluble in alcohol was treated with light petroleum as before, giving (*a*) a soluble fraction (48%), from which 6% of its weight of dihydroxybehenic acid, m. p. 132°, was obtained after saponification, and (*b*) an insoluble one (32%), giving 17% of its weight of the same acid when saponified. 6·5 G. of fraction (*b*) were extracted several times with hot 50% alcohol. The solution, after cooling at 0° for some days, deposited brassylic acid (0·3 g.), m. p. 111°, after purification. No brassylic semialdehyde was observed either before or after hydrolysis.

Oxidation of erucic acid at 70° *in the presence of acetic anhydride.* 10 G. of erucic acid in 20 g. of acetic anhydride with 0·6% of cobalt erucate were oxidised for 15 hours, fresh solvent being added from time to time. After 3 days the white solid formed was separated and gave oxidobrassidic acid, m. p. 70·8°. Yield, 12—15%. On hydrolysis with aqueous alcoholic hydrochloric acid, 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained.

The filtrate was poured into twice its weight of water, and sufficient ether added to dissolve the brown oil that separated. The solid deposited at 0° consisted of 13 : 14-dihydroxybehenic acid, m. p. 132°. Yield, 3%.

Oxidation of methyl erucate at 120° *in the presence of a catalyst.* 25 G. of methyl erucate with 0·6% of cobalt erucate were oxidised for 12 hours. 20 G. of the product were taken up with ether and extracted with potassium carbonate solution. The free oxidised acids obtained from the alkaline extract (15%) gave no pure compounds. The ethereal extract left 16·6 g. of oxidised esters, which were dissolved in 35 ml. of methyl alcohol and kept at 0° for 2 days. *Methyl oxidobrassidate* (2·6 g.) was deposited, giving 1·8 g. of the pure ester, m. p. 41·7°, I.V. 2 (Found: C, 74·9; H, 11·8. $C_{23}H_{44}O_3$ requires C, 75·0; H, 11·9%). Saponification gave oxidobrassidic acid, m. p. 70°.

The methyl-alcoholic filtrate contained 13·5 g. of residue, 3 g. of which were treated with alcoholic potassium hydroxide solution for 10 hours. The acids obtained on acidification were removed in ether (200 ml.) and from the solution 0·3 g. of dihydroxybehenic acid, m. p. 132°, was obtained.

Oxidation of methyl erucate at 70° *in the presence of a catalyst.* 25 G. of methyl erucate with 0·6% of cobalt erucate were oxidised similarly for 24 hours. 20 G. of the product in ether were extracted with potassium carbonate solution as above. The free oxidised fatty acids obtained (3·6 g.) could not be identified. The ethereal extract gave 15·2 g. of neutral oxidised esters, which were dissolved in 30 ml. of methyl alcohol, cooled to 0° for some days, and the liquid rapidly filtered. The solid, after purification, gave methyl oxidobrassidate (2·9 g.), m. p. 41·6° (Found: C, 74·8; H, 11·7%). After saponification oxidobrassidic acid, m. p. 70·5°, was obtained.

Oxidation of methyl erucate at 70° *in the presence of acetic anhydride and a catalyst.* 10 G. of methyl erucate in 20 ml. of acetic anhydride, with 0·06 g. of cobalt erucate, were oxidised in the same way, the volume being maintained by addition of acetic anhydride. After 12 hours the iodine value had fallen to 22. The solid product was removed and after purification consisted of methyl oxidobrassidate (2 g.), m. p. 41·8°.

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86. *Observations on the Absorption Spectra of Terpenoid Compounds. Part III. The Thiosemicarbazones of Irone, Eucarvone, and some Related Ketones.*

By A. E. GILLAM and T. F. WEST.

The analytical and absorption data for the pairs of thiosemicarbazones obtained from the *d*-irone of English and French origin (Gillam and West, *Nature*, 1941, **148**, 114; this vol., p. 95) indicate the possibility that these samples contain at least two ketones of different empirical formulæ. Further, in conformity with our earlier conclusion that irone is not a dienone like β-ionone but an αβ-unsaturated ketone like α-ionone, the irone thiosemicarbazones are found to exhibit absorption spectra similar to that of α-ionone thiosemicarbazone and different from that of the β-ionone derivative (cf. Ruzicka *et al.*, *Helv. Chim. Acta*, 1933, **16**, 1143; 1940, **23**, 935, 959; 1941, **24**, 1434).

The absorption spectra of the seven-membered ring dienone, eucarvone, and derived ketones and their semicarbazones and thiosemicarbazones are recorded and discussed.

THE various formulations envisaged by Ruzicka and his co-workers to explain the reactions and degradation products of irone have already been considered (Gillam and West, *loc. cit.*) in relation to the observed absorption spectra. While this account was in the press, Ruzicka, Seidel, and Firmenich (*Helv. Chim. Acta*, 1941, **24**, 1434) discussed their own absorption results and considered that structure (I) conformed best with all the available evidence. We therefore now record our accumulated absorption spectra data on the irone thiosemicarbazones and related compounds.

According to Ruzicka and his co-workers (*loc. cit.*), the irone of German origin yielded a thiosemicarbazone melting indefinitely at about 120° whereas this same sample after prolonged boiling with 20% sulphuric acid gave a derivative of m. p. 180°, not depressed by the sample prepared by Chuit (*Rev. Gén. Chim.*, 1903, **6**, 433). The analytical and absorption data obtained upon the thiosemicarbazones derived from samples of natural *d*-irone and the acid-treated product during the course of the present investigation and by earlier workers are summarised in Table I.

TABLE I.

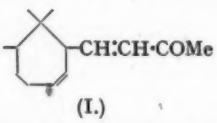
Analytical and Absorption Spectra Data for Irone Thiosemicarbazones.

Origin of parent irone.	Analysis (found), %. C.	H.	N.	M. p.	$\lambda_{max.}$	$\varepsilon_{max.}$	Mol. wt. taken.
German [1]	—	—	15·85	181°	—	—	—
Same product [2] recryst. by Ruzicka *et al.*	64·30	9·02	—	180°	—	—	—
German [2]	64·64	9·07	14·73	Turbid 110—120°, clear at 130°	—	—	—
German [3]	64·42	8·91	—	Turbid 120—122°, clear at 127°	2980	31,600	279
German [3] from irone boiled with 20% H_2SO_4	64·56	8·92	—	180°	3000	31,600	279
English [4]	64·6	8·4	15·2	185°	3020 2480	32,170 9,370	279
English [4]	65·7	8·9	14·75	112°, clear at 131°	3010 2465	32,450 10,520	293
French [4]	64·75	8·4	15·7	184—185°	3010 2470	32,860 10,460	279
French [4]	65·9	9·3	14·5	115°, clear at 130°	3010 2470	31,200 10,430	293
English from irone boiled with 20% H_2SO_4...	—	—	13·8[5]	156°	3050 2460	29,400 8,730	279

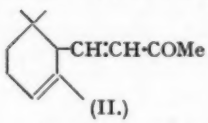
[1] Chuit, *loc. cit.* [2] Ruzicka, Seidel, and Schinz, *Helv. Chim. Acta*, 1933, **16**, 1143. [3] Ruzicka, Seidel, and Firmenich, *ibid.*, 1941, **24**, 1434. [4] Gillam and West, this vol., p. 95. [5] Insufficient material for complete purification.

Hence, the new data provide good analytical evidence for the presence in English and French irone of two ketones possessing different empirical formulæ. This is also supported by the light-absorption data, which show that the four semicarbazones are identical in the locations of their absorption bands; further, the values of the respective molecular extinction coefficients (ε) are approximately equal only when the several molecular weights indicated by the analytical data are used in their calculation (see Tables I and II).

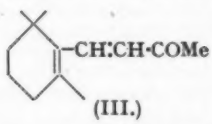
The possibility of the existence of isomeric ketones containing six- and seven-membered rings has been envisaged by Ruzicka, Schinz, and Seidel (*Helv. Chim. Acta*, 1940, **23**, 935, 959), but no evidence appears to have been advanced for the possible presence in natural irone of ketones possessing different empirical formulæ.



(I.)



(II.)



(III.)

Although we had but little irone available, we repeated Ruzicka's experiment on the effect of boiling the ketone with 20% sulphuric acid, and confirmed that the absorption spectrum of the irone changes in the sense that it develops a new absorption maximum near 3100 A. At first sight it might seem that the result of this treatment was an isomerisation to produce a dienone analogous to β-ionone (Ruzicka's β-irone). In our experiments, however, the recovered irone continues to change its light-absorbing properties spontaneously even after the sulphuric acid is removed, and it seems probable that several light-absorbing entities are produced and that some at least of these are labile and tend to disappear on standing. Further, the thiosemicarbazone obtained by us from the acid-treated irone (although not quite pure) absorbed at the same wave-length as the derivatives of the natural ketone. The light-absorption data for the various thiosemicarbazones are shown in Table II, and it will be seen that both irone itself and the acid-treated substance exhibit absorption spectra typical of similar compounds containing the C=C—C=N chromophore such as the thiosemicarbazone of α-ionone (II) in contrast to the compounds derived from β-ionone (III) and eucarvone (IV) which contain the C=C—C=C—C=N chromophore in a similar molecular environment.

In view of the possibility that irone may contain a seven-carbon skeleton (Ruzicka, Seidel, and Firmenich, *loc. cit.*), or alternatively that natural irone may contain a mixture of 7- and 6-carbon-ring isomers, the dienone

TABLE II.

Absorption Spectra of Thiosemicarbazones (in alcohol).

Parent ketone.	Thiosemicarbazone band. $\lambda_{max.}$	ε.	Thiosemicarbazide band. $\lambda_{max.}$	ε.	M. p. of thiosemicarbazone.	M.W. used.
C=C—C=N compounds.						
Irone [1] (German) [2]	3000	31,600	2450	11,700	clear at 127°	279
Irone [1] (acid-treated)	2980	31,600	2450	11,700	179—180°	279
Irone (English)	3020	32,170	2480	9,370	185°	279
Irone (English)	3010	32,450	2465	10,520	clear at 131°	293
Irone (French)	3010	32,860	2470	10,460	184—185°	279
Irone (French)	3010	31,200	2470	10,430	clear at 130°	293
α-Ionone	3025	36,500	2485	9,860	119—120°	265
1-Methyl-Δ[1]-*cyclo*hexen-3-one	3025[3]	30,350	2465	9,210	—	—
C=C—C=C—C=N compounds.						
β-Ionone	3140	31,370	2435	7,700	160—161°	265
Eucarvone	3310	22,750	2480	10,200	163—164°	223
Uncombined thiosemicarbazide [2]	—	—	2410	13,800	—	—

[1] Values taken from printed curves, therefore approximate only.
[2] Ruzicka, Seidel, and Firmenich, *loc. cit.*
[3] Unpublished data by Mr. L. K. Evans (Manchester University).

ketone eucarvone (IV), which is known to contain a 7-carbon-atom ring, provides an interesting model substance. Its absorption spectrum characteristics are given in Table III, and those of its semicarbazone and oxime on p. 486.

The numerical data on eucarvone compare well with published data on similar dienones and their derivatives (cf. Table III), and serve to emphasise the difference between these undoubted dienones and the major constituent of natural irone which has been shown to be an αβ-unsaturated ketone.

TABLE III.

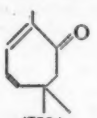
Absorption Spectra of Dienones (in alcohol).

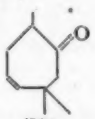
	Original ketone. $\lambda_{max.}$	ε.	Semicarbazone. $\lambda_{max.}$	ε.
Eucarvone	3035	6,300	3090	16,460
			2270	8,030
β-Ionone [1]	2935	8,700	2765	23,300
ψ-Ionone [1]	2910	21,800	2995	45,400
Citrylideneacetaldehyde [1]	2900	15,960	3045	47,200

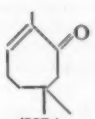
[1] Data by Burawoy (J., 1941, 23), who noted the exceptionally low value of the wave-length of maximum absorption for β-ionone semicarbazone.

On chemical evidence formula (V) was assigned by Wallach to the dihydroeucarvone obtained by reducing eucarvone with sodium and alcohol to dihydroeucarveol and oxidising this with chromic acid. The absorption spectrum confirms the absence of a conjugated system (see Experimental). On the other hand, structure (VI) was ascribed to the β-dihydroeucarvone obtained by reducing eucarvoxime with hydrogen in the presence of a palladium catalyst. The absorption spectrum of this compound clearly shows it to be an αβ-unsaturated ketone, and further, as a compound containing a disubstituted C=C—C=O chromophore, it should absorb at 2390 ± 50 A. (Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123). Its intense short-wave absorption band is actually situated at 2395 A., which makes it a very typical member of its class. This is of considerable interest, since the chromophore has a 7-carbon-atom ring whereas the rule was developed on data involving acyclic and 6-atom-ring compounds, and it has already been shown that at least two αβ-unsaturated ketones in a 5-carbon-atom-ring environment are exceptions to Woodward's rule (Gillam and West, J., 1941, 811, and unpublished observation).

The semicarbazone of β-dihydroeucarvone, is also perfectly typical of such derivatives of αβ-unsaturated ketones, absorbing as it does at 2645 A. (ε = 18,500).


(IV.)


(V.)


(VI.)

EXPERIMENTAL.

Analyses are by Drs. Weiler and Strauss, Oxford.

Irone Thiosemicarbazones.—The preparation of the four compounds has been described in this vol., p. 95.

α-Ionone Thiosemicarbazone.—A sample prepared according to Chuit's method (*loc. cit.*), after repeated recrystallisation, had m. p. 121—122° and showed maximum absorption at 3020 A. (ε = 31,600) and 2475 A. (ε = 9720). A purer

sample was obtained thus: α-ionone (1 g.) in ethyl alcohol (10 ml.) was added to a solution of thiosemicarbazide (0·7 g.) in water (5 ml.) containing a trace of hydrochloric acid. After being boiled under reflux (15 mins.), the solution was poured into cold water, and the thick oil extracted with ether. The ethereal solution was washed repeatedly with water, and the residue (1·6 g.) remaining after removal of the ether was extracted six times with light petroleum. The product (1·3 g.) had m. p. 104—108°, raised by two recrystallisations from aqueous methanol and two from light petroleum to 119—120°, unchanged by further recrystallisation (Found: N, 15·7. Calc. for $C_{14}H_{23}N_3S$: N, 15·85%). It showed maximum absorption at 3025 A. ($\varepsilon = 36{,}500$) and 2485 A. ($\varepsilon = 9860$).

β-Ionone Thiosemicarbazone.—A sample prepared according to Chuit (*loc. cit.*) had m. p. 160—161° (Chuit gives 158°) and showed maximum absorption at 3130 A. ($\varepsilon = 31{,}200$) and 2440 A. ($\varepsilon = 8150$), and another sample prepared as described for eucarvone thiosemicarbazone had m. p. 160—161° (Found: N, 15·6%) and displayed maximum absorption at 3150 A. ($\varepsilon = 31{,}540$) and 2430 A. ($\varepsilon = 7300$).

Treatment of Irone with Sulphuric Acid.—Irone (0·74 g.), derived from the English oil of orris (Gillam and West, this vol., p. 95), was refluxed for 10 hours in a nitrogen atmosphere, the oil extracted with ether, and the solution washed first with sodium bicarbonate and then with water. The ether was removed, and the oil distilled, giving 0·33 g. having b. p. 110—115°/2 mm., $n_D^{21\cdot5°}$ 1·5110, showing maximum absorption at 3100 A. ($\varepsilon = 3250$); after standing for 3 days the alcoholic solution gave a value of $\varepsilon = 2250$ at 2970 A., and after 7 days $\varepsilon = 1725$ at 2700—3000 A.

When treated with thiosemicarbazide according to the method of Ruzicka *et al.* (1933, *loc. cit.*) the bulk of the irone was recovered unchanged. Accordingly, recovered irone (0·21 g.) in methyl alcohol (7·5 ml.) was refluxed for 1 hour with a solution of thiosemicarbazide (0·15 g.) in water (2·5 ml.) in the presence of a trace of hydrochloric acid. When worked up as for α-ionone thiosemicarbazone, the crude thiosemicarbazone (0·06 g.) had m. p. 135° (sintering at 125°), raised by recrystallisation from methyl alcohol to 156° (sintering at 150°) (25 mg.) (Found: N, 13·8%). It showed maximum absorption at 3050 A. ($\varepsilon = 29{,}400$) (cf. Table I). When mixed with the thiosemicarbazone, m. p. 185°, the product melted at 176° (sintering at 162°).

The unreacted irone recovered during the light petroleum washing (0·075 g.) showed maximum absorption at 3100 A. ($\varepsilon = 4450$).

Eucarvone and its Derivatives.—The eucarvone was prepared from carvone according to Wallach's modifications (*Annalen*, 1905, **339**, 104) of Baeyer's method (*Ber.*, 1894, **27**, 810), and had b. p. 87—89°/7 mm., $n_D^{22°}$ 1·5085, $d_{15}^{22°}$ 0·9056, $\alpha_D + 1·5°$; it showed maximum absorption at 3035 A. (alcohol) ($\varepsilon = 6000$). The semicarbazone (Baeyer, *loc. cit.*), m. p. 185—186°, showed maximum absorption at 3090 A. ($\varepsilon = 16{,}460$) and 2270 A. ($\varepsilon = 8030$); the eucarvone regenerated from it as described by Wallach had b. p. 85—86°/5 mm., $n_D^{20°}$ 1·5100, $\alpha_D \pm 0°$ (*c*, 5 in alcohol); $\lambda_{max.}$ 3035 A. (alcohol) ($\varepsilon = 6300$).

Eucarvone (1·8 g.) in ethyl alcohol (20 ml.) was added to a solution of thiosemicarbazide (1·25 g.) in water (10 ml.) containing a trace of hydrochloric acid, the solution refluxed for 5 hours, poured into water, and the precipitated thiosemicarbazone extracted with ether. Removal of the solvent from the dried ethereal solution gave a solid (2·1 g.), m. p. 154—156°; after recrystallisation from methyl alcohol, the white crystalline *eucarvone thiosemicarbazone* (1·2 g.) has m. p. 163—164°, unchanged by further recrystallisation (Found: N, 19·1. $C_{11}H_{17}N_3S$ requires N, 18·9%). This sample showed maximum absorption at 3310 A. (alcohol) ($\varepsilon = 22{,}750$) and 2480 A. ($\varepsilon = 10{,}200$).

The Dihydroeucarvones.—Eucarvone was reduced to dihydroeucarveol and this was oxidised to dihydroeucarvone with chromic acid (Baeyer, *Ber.*, 1894, **27**, 1915; Wallach, *Annalen*, 1899, **305**, 239). The semicarbazone, after repeated recrystallisation from methyl alcohol, had m. p. 190—191° and was used to regenerate the α-dihydroeucarvone by steam-distillation in the presence of phthalic acid. This had b. p. 44—45°/0·5 mm., $n_D^{17°}$ 1·4671, $d_{15}^{20°}$ 0·938, and showed maximum absorption at 2910 A. ($\varepsilon = 33$), the band being typical, in both location and intensity, of an unconjugated carbonyl group.

Eucarvoxime, m. p. 106°, prepared as described by Wallach (*ibid.*), showed maximum absorption at 2920 A. ($\varepsilon = 10{,}500$). It was reduced in the presence of a colloidal palladium catalyst (Paal) and treated as described by Wallach (*Annalen*, 1914, **403**, 91). The semicarbazone of the ketone obtained had m. p. 201°, and showed maximum absorption at 2645 A. ($\varepsilon = 18{,}500$); it was used to regenerate β-dihydroeucarvone by steam-distillation in the presence of dilute sulphuric acid. This had b. p. 54°/1·5 mm., $n_D^{23°}$ 1·4793, and showed maximum absorption at 2395 A. ($\varepsilon = 7250$) and 3080 A. ($\varepsilon = 137$).

Determinations of absorption spectra were made on a Hilger E_3 quartz spectrograph in conjunction with a Spekker photometer, standard methods being used.

THE UNIVERSITY, MANCHESTER.
STAFFORD ALLEN AND SONS, LTD., LONDON, N. 1. [*Received, May 8th*, 1942.]

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87. *Observations on the Absorption Spectra of Terpenoid Compounds. Part IV. Five-atom-ring Unsaturated Ketones.*

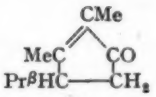
By A. E. GILLAM and T. F. WEST.

Absorption data are recorded for the five-atom-ring compounds dihydrojasmone and tetrahydropyrethrolone and their semicarbazones. The data on the first two compounds are not in accord with Woodward's generalisation (*J. Amer. Chem. Soc.*, 1941, **63**, 1123) covering the absorption spectra of αβ-unsaturated ketones. These results and the anomalous case of *iso*thujone previously reported (Gillam and West, J., 1941, 811) are therefore best explained by the specific effect due to the five-atom-ring environment as compared with C=C—C=O compounds in acyclic and six-atom-ring systems. On the other hand the seven-atom-ring compound β-dihydroeucarvone (V) (Gillam and West, preceding paper) falls into line with the six-atom-ring and acyclic compounds.

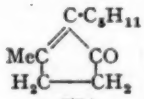
IT has been shown that the absorption spectra of αβ-unsaturated ketones fall regularly into three classes depending on whether the C=C—C=O chromophore has one, two, or three non-absorbing substituents (Woodward, *loc. cit.*); for instance, trisubstituted αβ-unsaturated ketones absorb maximally at 2540 ± 50 A. Exceptionally, it has been found (Gillam and West, *loc. cit.*, 1941) that *iso*thujone (I) prepared by the isomerisation of thujone with sulphuric acid shows maximum absorption at 2370 A. ($\varepsilon = 13{,}500$), whereas the lævorotatory form prepared from sabinol by hydrogenation and subsequent oxidation (Short and Read, J., 1939, 1043) shows an even greater divergence ($\varepsilon = 6180$ at 2310 A.).

More recently Woodward (*J. Amer. Chem. Soc.*, **1942**, **64**, 76) has reconsidered the data on trisubstituted αβ-unsaturated ketones and finds that the best average position of the band is at 2470 ± 50 A. when there is no exocyclic double bond and at 2520 ± 50 A. with one exocyclic ethylene linkage.

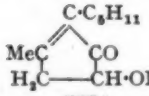
In view of the anomalous position of *iso*thujone, we have examined two other five-atom-ring unsaturated ketones in order to determine whether this molecular environment normally produces a hypsochromic effect on the location of the *K*-band in the absorption spectrum, and if so, whether there is any constancy in the effect.



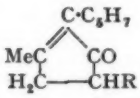
(I.)
*iso*Thujone.



(II.)
Dihydrojasmone.

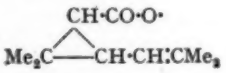


(III.)
Tetrahydropyrethrolone.

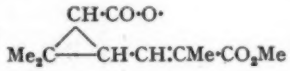


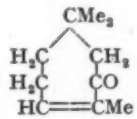
(IV.)

Pyrethrin-I, R =



Pyrethrin-II, R =





(V.)
β-Dihydroeucarvone.

Dihydrojasmone was prepared by the catalytic reduction of a mixture of pyrethrins-I and -II (IV), described by LaForge and Haller (*J. Org. Chem.*, **1937**, **2**, 49), and the ketone regenerated from the semicarbazone of appropriate melting point. Two samples of tetrahydropyrethrolone, (*a*) and (*b*), were examined; they were obtained (*a*) by the reduction of pyrethrolone (IV, R = OH) semicarbazone obtained from a semicarbazone predominantly derived from pyrethrin-I, and (*b*) from pure pyrethrin-II semicarbazone.

The absorption spectra of the five-atom ring ketones and their semicarbazones are shown in the following table.

Absorption data for solutions in alcohol.

	K-Band.		*R*-Band.	
	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
*iso*Thujone (I) [1]	2375	12,000	(3100)	80
l-2 : 3-Dimethyl-4-*iso*propyl-Δ²-*cyclo*pentenone [1,2]	2310	6,180	3100	35
Dihydrojasmone (II)	2370	12,200	3040	55
Tetrahydropyrethrolone (III) (*a*)	2320	11,540	3120	64
Tetrahydropyrethrolone (III) (*b*)	2320	12,700	not determined	
*iso*Thujone semicarbazone [1]	2670	24,800	absent	
Dihydrojasmone semicarbazone	2665	20,400		
Tetrahydropyrethrolone semicarbazone (*a*), *ex* pyrethrin-I	2650	22,500		
Tetrahydropyrethrolone semicarbazone (*b*), *ex* pyrethrin-II	2650	21,770		

[1] Gillam and West, J., 1941, 811.
[2] The low value of both $\lambda_{max.}$ and $\varepsilon_{max.}$ here may be due to the specimen's not being pure.

Woodward's amended average value of 2470 ± 50 A. being taken for trisubstituted six-atom-ring and acyclic αβ-unsaturated ketones, the deviations of the three five-atom-ring ketones from this value are as follows (for alcoholic solutions):

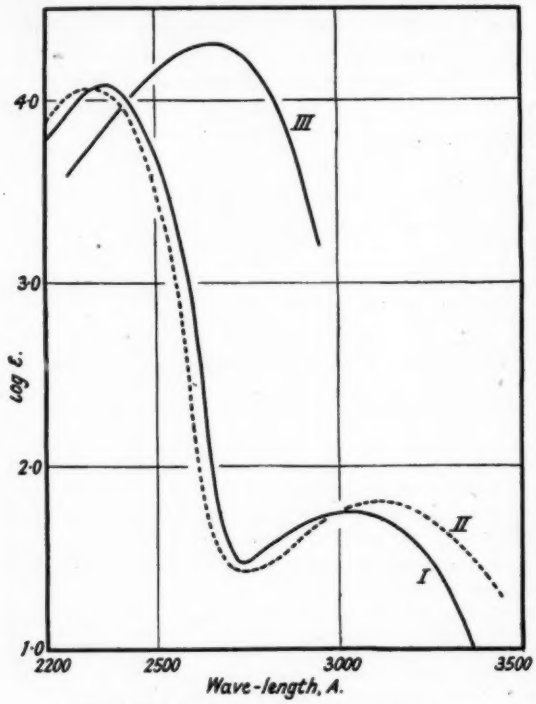
	$\lambda_{max.}$, A., obs.	Deviation for five-atom-ring environment, A.
*iso*Thujone	2375	− 95
Dihydrojasmone	2370	−100
Tetrahydropyrethrolone	2320	−150
Mean	2355 ± 35	

The mean value for these compounds thus differs from that obtained on analogous six-atom-ring and acyclic compounds by approximately −110 A., and this decrement can be used as an amendment to Woodward's rule when a five-atom-ring system is suspected or known to be present. In this connection it has already been noted that *cyclo*pentadiene is anomalous among other dienes (Booker, Evans, and Gillam, J., **1940**, 1453) in that it absorbs maximally at 2385 A. (Scheibe, *Ber.*, **1926**, **59**, 1333), whereas the corresponding six-atom-ring diene, Δ¹·³-*cyclo*hexadiene (cf. Allsopp, *Proc. Roy. Soc.*, **1934**, *A*, **143**, 618), absorbs at 2560 A., *i.e.*, a difference of −175 A.

It is now highly probable that the explanation of the abnormally short wave-length of the maximum in the absorption spectrum of *iso*thujone previously reported (see above) lies in the effect of the five-atom-ring environment on the position of the absorption band. The alternative suggestion that the accepted structure (I) was open to doubt must now be withdrawn.

The hypsochromic effect of the five-atom-ring structure being thus evident in at least three compounds, it is interesting to notice that the only authentic αβ-unsaturated ketone in a seven-atom ring (β-dihydro-

eucarvone) for which the location of the *K*-band has been recorded (Gillam and West, preceding paper) is quite typical of similar acyclic and six-atom-ring compounds, having $\lambda_{max.}$ 2395 A.



Absorption spectra of alcoholic solutions of:

I. *Dihydrojasmone.*
II. *Tetrahydropyrethrolone.*
III. *Dihydrojasmone semicarbazone.*

EXPERIMENTAL.

(Carbon and hydrogen determinations are by Drs. Weiler and Strauss, Oxford.)

Dihydrojasmone.—A concentrated extract of pyrethrum (7·83 g.), prepared essentially as described by LaForge and Haller (*J. Amer. Chem. Soc.*, 1935, **57**, 1893) and containing, by the Wilcoxon method, pyrethrin-I 55·7%, pyrethrin-II 7·3%, was reduced in alcoholic solution in the presence of a platinum oxide catalyst and absorbed 1547 ml. hydrogen at N.T.P. The mixture of dihydrojasmone and hexahydropyrethrone was then isolated (2·1 g.) and converted into the semicarbazone as described by Haller and LaForge (*loc. cit.*, 1937). The dihydrojasmone semicarbazone (0·62 g.) obtained by fractional crystallisation from alcohol had m. p. 165° (sintering at 160°), and after two recrystallisations from benzene, m. p. 175—176°. It showed maximum absorption at 2665 A. (ε = 20,400). The dihydrojasmone regenerated by steam distillation in the presence of potassium bisulphate (Staudinger and Ruzicka, *Helv. Chim. Acta*, 1924, **7**, 245) had b. p. 75—76°/1 mm., $n_D^{21°}$ 1·4800, and showed maximum absorption at 2370 A. (ε = 12,200) and at 3040 A. (ε = 55) (Found: C, 79·4; H, 11·0. Calc. for $C_{11}H_{18}O$: C, 79·5; H, 10·8%).

Tetrahydropyrethrolone.—The preparation of pyrethrolone semicarbazone will be considered elsewhere. A sample (3·5 g.), m. p. 210—211° (decomp.), obtained from practically pure pyrethrin-I semicarbazone, m. p. 113° (sintering at 103°), by treatment with a solution of sodium methoxide, was dissolved in ethyl acetate–methyl alcohol and hydrogenated in the presence of a platinum oxide catalyst (Haller and LaForge, *J. Org. Chem.*, 1936, **1**, 50); 682 ml. of hydrogen (N.T.P.) were absorbed. The crude tetrahydropyrethrolone semicarbazone (3·2 g.) had m. p. 178—180°, raised to 193—194° by three recrystallisations from acetone (Found: C, 60·0; H, 8·8. Calc. for $C_{12}H_{21}O_2N_3$: C, 60·25; H, 8·8%). It showed maximum absorption at 2650 A. (ε = 22,500). The tetrahydropyrethrolone regenerated in the presence of cold potassium bisulphate solution (LaForge and Haller, *J. Amer. Chem. Soc.*, 1936, **58**, 1779) had b. p. 135°/1 mm., $n_D^{20°}$ 1·4930, $[\alpha]_D$ +11·5° (*c*, 2·777 in alcohol) and showed maximum absorption at 2320 A. (ε = 11,540) and at 3120 A. (ε = 64) (Found: C, 73·0; H, 9·8. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 9·9%).

Pyrethrolone semicarbazone (1·93 g.), m. p. 212—213° (decomp.), obtained *via* pyrethrin-II semicarbazone, m.p. 164—165°, and treated as described above, absorbed 379 ml. of hydrogen at N.T.P. The crude tetrahydro-compound (1·98 g.) melted at 176° and after three recrystallisations had m. p. 196° and showed maximum absorption at 2650 A. (ε = 21,770) (Found: C, 60·0; H, 8·7%). The ketone regenerated from this sample had b. p. 142—143°/1·5 mm., $n_D^{19°}$ 1·4911, $[\alpha]_D$ + 17·7° (*c*, 0·935 in alcohol) and displayed maximum absorption at 2320 A. (ε = 12,700) (Found: C, 72·1; H, 9·8%).

Absorption-spectra determinations were carried out in purified ethyl alcohol by means of a Hilger E_3 quartz spectrograph and a Spekker photometer.

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88. *Long-chain Acids containing a Quaternary Carbon Atom. Part I.*

By A. J. BIRCH and Sir ROBERT ROBINSON.

A preliminary survey has been made of the methods applicable to the synthesis of acids of varied constitution containing a quaternary carbon atom, and a number of substances of this type have been prepared. Their characteristic behaviour in mono-layer films and their biological effects will be described later.

VERY few branched-chain fatty acids have been found in nature and most of those known are related to terpenoid compounds. The oils of *Hydnocarpus* and related species contain, however, a number of acids characterised by the presence of a *cyclo*pentene ring. The naphthenic acids from petroleum (cf. "The Science of Petroleum," Oxford, 1938, **2**, 1013) are mainly homologous compounds, containing a trimethyl*cyclo*pentane ring, but some are straight-chain acids with attached methyl groups. Another important series of branched-chain fatty acids has recently been isolated by Anderson and co-workers from *Mycobacterium Lepræ* and *M. Tuberculosis*, and some of the compounds were thought to be the characteristic toxins of the organisms (*J. Biol. Chem.*, 1927, **74**, 537; 1929, **83**, 169; 1930, **85**, 77; 1932, **97**, 619; 1932, **98**, 43; 1934, **106**, 87; 1936, **113**, 637; 1936, **114**, 431, 467; and later papers). Sabin (*J. Exp. Med.*, 1927, **46**, 645) showed that Anderson's phthioic acid (from *M. Tuberculosis*) produces local lesions on injection, similar in character to those produced by the living organism, but it now seems possible that it is a breakdown product of the true toxin, which is an

acid $C_{60}H_{120}(CO_2H)(CH_2{\cdot}OH)$, active in doses of only 0·002 mg., and produces lesions away from the site of injection, *e.g.*, in the lungs (Chocroun, *Compt. rend.*, 1940, **210**, 749).

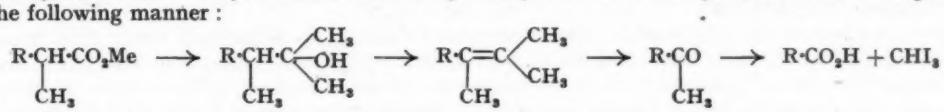
Many synthetic branched-chain acids have been synthesised, especially by Adams and his co-workers (*J. Amer. Chem. Soc.*, 1925, **47**, 2727; 1926, **48**, 1080, 1089, 2385, 2393, 2444; 1927, **49**, 2934, 2940; 1928, **50**, 1475, 1503, 1983, 2297; 1929, **51**, 1261), but since the malonic ester method was almost invariably used, the acids have been of the mono- or di-substituted-acetic acid type. Only one or two long-chain acids containing quaternary carbon atoms have been described.

Phthioic Acid.—Anderson (*loc. cit.*) isolated the branched-chain acids from *M. Tuberculosis* by first extracting fatty material with a mixture of alcohol and ether, and then separating the fraction soluble in acetone. The acids produced by saponification, when submitted to a lead salt–ether separation, gave lead palmitate with a little stearate and cerotate, and the soluble lead salts of a mixture of acids. These were hydrogenated, and again separated by solution of the lead salts in ether. The soluble portion contained the salts of a mixture of saturated fatty acids which were esterified, and fractionated, giving esters corresponding to an acid $C_{19}H_{38}O_2$, tuberculostearic acid, which had no physiological action, an acid, $C_{26}H_{52}O_2$, phthioic acid, which was toxic, and some higher acids which were not fully investigated.

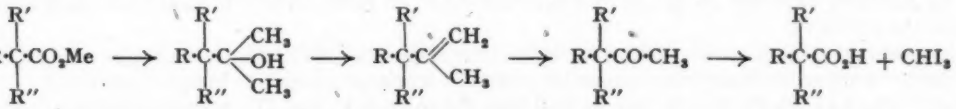
The purest specimens of phthioic acid had m. p. 20—21° and were optically active. Analysis of the acid itself, and of crystalline derivatives, established the formula $C_{26}H_{52}O_2$; it may be derived from some unsaturated precursor. The degradation of phthioic acid has not shed much light on the structure of the substance. Wagner-Jauregg (*Z. physiol. Chem.*, 1937, **247**, 135) obtained a maximum of 2·41 mols. of acetic acid in a Kuhn–Roth determination, compared with a value of 1·41 for tuberculostearic acid. Apart from the possibility of a larger number of *gem*-dimethyl groups, this demonstrated that phthioic acid has three, or at most four, chains in the molecule. Chargaff (*Ber.*, 1932, **65**, 745) synthesised a number of C_{26} acids of the form $RR'CH{\cdot}CO_2H$, and from a study of their m. p.'s arrived at the same conclusion.

Spielman and Anderson (*J. Biol. Chem.*, 1935—36, **112**, 759) oxidised phthioic acid by means of chromic acid in acetic acid solution. They obtained a saturated fatty acid, $C_{11}H_{22}O_2$, which was stated to differ from *n*-undecoic acid in that the derivatives had lower m. p.'s. They therefore concluded that it had a branched chain but in view of the small amount available, and the difficulty of separating close homologues, the identity of this C_{11} acid must still be regarded as an open question.

Spielman and Anderson also attempted to determine the nature of the alkyl groups adjacent to the carboxyl by treating methyl phthioate with methylmagnesium iodide, dehydrating the tertiary alcohol formed, and oxidising the hydrocarbon. They obtained what they thought to be a methyl ketone, and interpreted their results in the following manner:



The experimental evidence is not convincing and these results can be interpreted in other ways, for example:



Spielman and Anderson found the chlorination of the acid by phosphorus pentachloride to be gradual and progressive and no clear deduction from the experiment was possible.

These workers stated their conclusions as follows: "Phthioic acid possesses a branched chain, probably with methyl groups in the α-position, and in the neighbourhood of the eleventh carbon atom."

Since purely chemical methods had proved inconclusive, Stenhagen (private communications) turned his attention to physical methods. Chibnall and Piper (*Biochem. J.*, 1934, **28**, 2189, etc.; cf. Francis, *Proc. Roy. Soc.*, 1930, *A*, **128**, 214; Shearer, *Proc. Roy. Soc.*, 1925, *A*, **108**, 655) have used the method of *X*-ray reflection from crystalline layers with signal success in the examination of long-chain substances from waxes, but it was found that suitable layers could not be obtained from phthioic acid. Stenhagen succeeded, however, in building multilayer films of barium phthioate. Examination of these by *X*-ray reflection gave for the molecule a length of between twelve and fourteen carbon atoms.

Stenhagen next turned his attention to surface films of the substance on water, and found that it formed a monolayer film different in type from that of any known fatty acid, and in particular behaved quite differently from disubstituted acetic acids, *e.g.*, decyldodecylacetic acid, collapsing at an area of about 38 A.², compared with a value of about 60 A.², and having a considerably higher surface dipole moment. Since the area of one highly compressed chain is about 18—20 A.², he concluded that the molecule contains two long chains, and postulated in addition the presence of an ethyl or methyl group in the neighbourhood of the carboxyl, which would have the effect of causing the chains to adhere more readily. Owing to the comparatively large value of the optical rotation he considered an ethyl group more likely than a methyl, and, of course, the chains must be unequal to permit of activity at all. He considered the most likely formulation to be ethyldecyldodecylacetic acid.

The main problem has therefore been the synthesis of this, or related substances, and an examination of their

film properties and physiological behaviour. Although this object has not yet been completely attained, a number of trisubstituted acetic acids and trisubstituted propionic acids have been prepared and studied. As we do not wish to anticipate unpublished results of Stenhagen, we refrain from giving full details at this stage but our results are in harmony with those of the Swedish author so far as we know them. They are, briefly, that the films of the trialkylacetic and βββ-trialkylpropionic acids collapse at a much smaller area than those of the disubstituted acids, approximating to phthioic acid in their behaviour. Stenhagen (*loc. cit.*) obtained the collapse areas of the disubstituted acetic acids by rapidly compressing the film to a pressure of some 20 dynes, when values of about 60 A.^{2} were found. We found that the films begin to collapse at about 12 dynes, and that it was impossible to obtain reproducible curves above that pressure, the area being then about 75 A.^{2}. The trisubstituted acids, however, give definite, almost flat, collapse points, at about 11 dynes and 40 A.^{2} in the case of the straight chain acids, and 60 A.^{2} in the case of β-methyl-β-(β′-*cyclo*hexylethyl)-β-decylpropionic acid. Trialkylcarbinols, such as methyldioctylcarbinol, give very similar curves, but the dialkylcarbinols do not form stable films.

All our film measurements were made on N/100-sulphuric acid, with the type of apparatus designed by Professor N. K. Adam, and modified by Dr. G. I. Jenkins, whose kind assistance the authors gratefully acknowledge.

The results of biological tests are not yet available in full. Stenhagen, however, has stated that dimethyldecylacetic acid produces toxic symptoms on injection into the peritoneum of rabbits, and that methyldioctylacetic acid produces toxic cell reactions. He also reported that 3-methyl-3-octylundecoic acid has no toxic or irritant properties on injection. It is, therefore, of interest that its antiseptic potency against *M. Tuberculosis* is at least as great as that of the C_{20} acids studied by Adams and Stanley. It is hoped that a report on the bactericidal properties of these and other similar acids that may be synthesised will be published in due course by our biological collaborators. This work is in its initial stages at the present time and all that can be said is that several of the branched-chain acids exhibit bactericidal potency which is, however, surpassed by that of certain other types of synthetic agents. This does not discourage us because it seems possible that the aliphatic compounds may be useful auxiliaries, and it is certainly necessary to explore their potentialities.

Synthetical Methods.—Variants of direct alkylation processes are available for the synthesis of trisubstituted acetic acids and the method of Hudson and Hauser (*J. Amer. Chem. Soc.*, 1940, **62**, 2457), published during the course of the present work, may prove of great value. It works best with disubstituted acetic esters, which are treated with sodium triphenylmethyl and an alkyl halide in ethereal solution (cf. Schlenk, Hillemann, and Rodoff, *Annalen*, 1931, **487**, 147).

Aliphatic nitriles can be alkylated by the method of Ziegler (G.P. 570,594 of 1931; 581,728 of 1933, cf. Bockmühl and Ehrhardt, G.P. 622,875 of 1934), and in this way we have prepared n-*octyl*-n-*nonylacetonitrile* from undeconitrile and octyl bromide in the presence of sodamide and *methyldi*-n-*decylacetonitrile* from propionitrile and decyl bromide under similar conditions. The former could be hydrolysed to an *amide*, but the latter was unchanged after having been submitted to the most vigorous of hydrolytic agents. Incidentally the lack of difficulty experienced in the hydrolysis of esters of phthioic acid is hard to explain on the basis of Stenhagen's suggestions.

Haller's method (*Compt. rend.*, 1909, **148**, 127; 1909, **149**, 5) of alkylation of acetophenone and subsequent decomposition of the ω-trialkylacetophenone by sodamide was applied by him to the synthesis of 2 : 2-dimethyllauric acid,* $CH_3{\cdot}[CH_2]_9{\cdot}CMe_2{\cdot}CO_2H$, but we find that the m. p. is 4°, not 27°, and the specimens of higher m. p. (which we also obtained in the first instance) contained unchanged amide.

We were able to prepare 2 : 2-*dimethylstearic acid* in a similar fashion, but all attempts to alkylate acetophenones substituted in the ω-position by two long-chain alkyls were unsuccessful. For example, we were unable to methylate ωω-*di*-n-*decylacetophenone*, itself prepared by applying the Friedel–Crafts reaction to benzene and di-*n*-decylacetyl chloride. A number of new long-chain *tert.*-alcohols have been prepared and several methods for the replacement of hydroxyl by carboxyl have been studied; none of them proved of great interest.

Whitmore and Badertscher (*J. Amer. Chem. Soc.*, 1933, **55**, 1550) prepared Grignard reagents from *tert.*-alkyl chlorides up to dimethyl-*n*-amylcarbinyl chloride. In this case the yield of carboxylic acid obtained by reaction with carbon dioxide was 22%. We were unable, however, to prepare an organo-magnesium compound from methyldi-*n*-decylcarbinyl chloride, either alone or in the presence of an equivalent of methyl iodide, or of magnesium iodide. Synthesis of nitriles from the carbinols (cf. Butlerow, *Annalen*, 1873, **165**, 323) is a process known to give poor yields and such nitriles are more easily made by direct alkylation.

Reichstein, Rosenberg, and Eberhardt (*Helv. Chim. Acta*, 1935, **18**, 721) condensed *tert.*-alkyl chlorides with methyl furoate in presence of aluminium chloride and later oxidised away the furan nucleus. The result of applying this process to methyldiheptylcarbinyl chloride and to methyldioctylcarbinyl chloride was that small quantities of acids were obtained, apparently of the anticipated nature, but in view of the possibility of isomeric change in the alkyl groups (cf. Gilman and Turck, *J. Amer. Chem. Soc.*, 1939, **61**, 473) we do not feel confident that the products are homogeneous. A specimen of 2 : 2-dimethyl-lauric acid made in this way was certainly not quite pure. Anschütz (*Annalen*, 1903, **327**, 406) obtained trimethylacetic acid by the oxidation of *tert.*-butylphenol and we tried to improve this type of method by employment of a catechol derivative.

4-αα-*Dimethylundecylveratrole* (I) was obtained in good yield by the condensation of dimethyl-*n*-decyl-

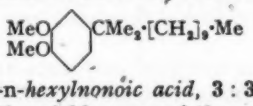
* The carboxyl group of the normal fatty acids is numbered 1 in this communication.

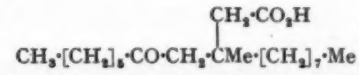
carbinyl chloride with veratrole in the presence of aluminium chloride, and the corresponding dihydric phenol was oxidised with some difficulty to 2 : 2-dimethyl-lauric acid. Methyldi-*n*-heptylcarbinyl chloride gave, however, a very mixed product in the first stage. It seems that a generally applicable procedure for the conversion of *tert.*-alcohols, including more than one long-chain group, into corresponding carboxylic acids is not yet available.

A very direct route to ethyldialkylacetic acids would be opened up if the disubstituted acetoacetic esters could be reduced. The reduction of ethyl acetoacetate to ethyl butyrate has been reported by Vavon (*Ann. Chim.*, 1914, [ix], **1**, 179; cf. Sabatier and Mailhe, *ibid.*, 1909, [viii], **16**, 78) and by Steinkopf and Wolfram (*Annalen*, 1923, **430**, 113), but we found that the *C*-di-*n*-nonyl derivative was highly resistant to reducing agents and was recovered unchanged in all our experiments. In this case there is doubtless a powerful protection of the carbonyl group by the neighbouring long chains and better success was to be anticipated if the carbonyl group were placed in the γ- or δ-position to the alkyl substituents.

The methods to which we have paid most attention are based on the use of αα-dialkylsuccinic and ββ-dialkylglutaric acids as intermediates and also the application of the Michael reaction to appropriate αβ-unsaturated ketones. The preparation of the substituted succinic and glutaric acids was effected by known methods, essentially those of Higson and Thorpe (J., 1906, **89**, 1455) and Lapworth and McRae (J., 1922, **121**, 2741) for the former and of Guareschi (*Atti R. Accad. Sci. Torino*, 1900—1, **36**, 443 and later papers) and Thole and Thorpe (J., 1911, **99**, 440) for the latter. The ketones employed as starting points were *n*-hexyl, *n*-octyl, and *n*-decyl methyl ketones and it seems that these methods succeed only with methyl ketones; for instance, ethyl *n*-decyl ketone did not undergo the Guareschi reaction, nor could it be condensed with cyanoacetamide in the presence of piperidine (cf. Thole and Thorpe, *loc. cit.*). This sets a limit to the general applicability of these methods; one of the substituting groups must be methyl. The necessary modifications of detail are described in the experimental section, but mention may be made of the excellent device of Cope (*J. Amer. Chem. Soc.*, 1937, **59**, 2327), of which advantage was taken in effecting the condensation of the ketones with ethyl cyanoacetate in the presence of piperidine. The ββ-dialkylglutaric anhydrides were converted into semi-esters by reaction with alcohol, and then into ester chlorides. The ester chlorides made from the αα-dialkylsuccinic anhydrides in this way would not be of the desired structure and in this case it was necessary to resort to partial hydrolysis of the esters (cf. Bone, Sudborough, and Sprankling, J., 1904, **85**, 534). In this way intermediates of the type $CO_2Et{\cdot}CRR'{\cdot}CH_2{\cdot}COCl$ were secured.

The keto-acid synthesis of Robinson and Robinson (J., 1925, **127**, 175; 1930, 745; 1934, 1543) has been used in several examples, but it did not give good results with acylacetoacetic esters in which the acyl group is derived from succinic or glutaric acid. As an example the ester chloride from β-methyl-β-octylglutaric acid was condensed with ethyl sodio-2-acetylheptoate, and the product hydrolysed to *5-keto-3-methyl-3-n-octylundecoic acid* (II). This acid was reduced by Clemmensen's method, and a small quantity of unchanged material removed by esterification and treatment with alcoholic sodium ethoxide, which converted the keto-ester into an alkali-soluble dihydroresorcinol derivative.

(I.) 

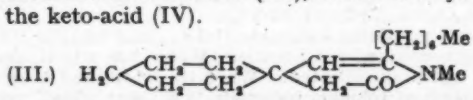

(II.)

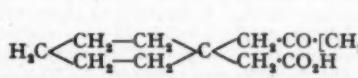
3-Methyl-3-n-hexylnonoic acid, 3 : 3-*dimethylundecoic acid*, and 3 : 3-*dimethyltetradecoic acid* were prepared in this way; the yields were of the order 10—15% and the recovery of the more valuable starting material was inadequate compensation.

Reaction of the ester chlorides with zinc alkyls (cf. Blaise and Koehler, *Compt. rend.*, 1909, **148**, 489; *Bull. Soc. chim.*, 1910, **7**, 215) gave improved results and this method is much the more direct though also not of general applicability. The use of organo-cadmium compounds (Gilman, *Rec. Trav. chim.*, 1936, **55**, 518) was tried, also with success, but the yields were somewhat inferior to those obtained with the zinc derivatives.

The ester chloride from β-methyl-β-*n*-octylglutaric acid reacted with *n*-heptylzinc chloride, with formation of the ester of *5-keto-3-methyl-3-n-octyl-lauric acid* [homologue of (II)].

We were unable to employ the interaction of Grignard agents and acid anhydrides in the long-chain series (cf. Weizmann and Bergmann, J., 1936, 567; 1938, 1147; Guha, *Ber.*, 1938, **71**, 2671), but the method of Lukeš (*Coll. Czech. Chem. Comm.*, 1929, **1**, 119; 1936, **8**, 223) gave more promise. This consists in the hydrolysis of the product of interaction of an *N*-substituted cyclic imide with an organo-magnesium compound, whereby keto-acids are produced. For example, cyclo*hexane*-1 : 1-*diacetomethylimide* and *n*-heptylmagnesium bromide furnished the intermediate (III), which on hydrolysis with concentrated hydrobromic acid was converted into the keto-acid (IV).

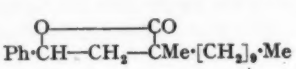
(III.) 

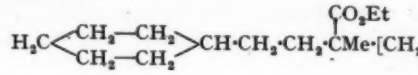

(IV.)

Since the work of Adams and Stanley (*loc. cit.*) showed that the presence of a *cyclo*hexyl group in the fatty acid molecule was consistent with antiseptic activity against *B. Leprae*, we extended the work in this direction. Phenyl-keto-acids were obtained in good yield from the substituted succinic and glutaric anhydrides in the presence of aluminium chloride under remarkably mild conditions. Examples are (V) from α-methyl-α-*n*-decylsuccinic anhydride and (VI) from β-methyl-β-*n*-hexylglutaric anhydride.

V.) $Ph{\cdot}CO{\cdot}CH_2{\cdot}CMe(CO_2H){\cdot}[CH_2]_9{\cdot}Me$ $Ph{\cdot}CO{\cdot}CH_2{\cdot}CMe(C_6H_{13}){\cdot}CH_2{\cdot}CO_2H$ (VI.)

The reduction of (V) by Clemmensen's method proceeded slowly and furnished a mixture of products, from which two isomeric forms of the lactone (VII) were isolated.

(VII.) 

 (VIII.)

Saturated esters, *e.g.*, (VIII) from the ester of (V), were obtained directly by pressure hydrogenation over Raney nickel (cf. Adkins, "Reactions of Hydrogen," Wisconsin Univ., 1937, p. 71).

Self-condensation products of methyl *n*-amyl ketone and methyl *n*-decyl ketone were obtained by following the noteworthy procedure of Colonge (*Bull. Soc. chim.*, 1933, [iv], **53**, 282; 1934, [v], **1**, 1101; 1938, **5**, 98, 155) in which methylanilinomagnesium bromide is used as the condensing agent in ethereal solution. The product from methyl amyl ketone was shown to be n-*amyl* β-n-*amyliso*propenyl ketone (IX) and that from methyl decyl ketone is doubtless analogously constituted. Reaction with ethyl sodiomalonate in boiling alcoholic solution

(IX.) $Me\cdot[CH_2]_4\cdot CMe{:}CH\cdot CO\cdot[CH_2]_4\cdot Me$ $\qquad$ $R\cdot CH_2\cdot CMe\langle^{CH(CO_2Et)\cdot CO}_{CH_2\text{——}CO}\rangle CHR$ (X.)

furnished the substituted diketo-esters of the form (X; R = C_4H_9 or C_9H_{19}) and these were readily hydrolysed and decarboxylated to the corresponding substituted dihydroresorcinols. The latter compounds could not be hydrolysed to keto-acids and it was therefore necessary to avoid the formation of the ring in the first place. This was accomplished by the use of sodiocyanoacetamide instead of ethyl sodiomalonate. The crystalline compounds (XI; R = C_5H_{11} or $C_{10}H_{21}$) were thus obtained and hydrolysis to the keto-acids (XII) was smoothly effected by a boiling mixture of sulphuric and acetic acids with water. Hydrolysis by alkalis (cf. Qudrat i Khuda, J., 1929, 715) was much less satisfactory; it brought about reversal of the Michael addition to some extent and the later decarboxylation stage gave ketodilactone in addition to the keto-acid.

(XI.) $R\cdot CO\cdot CH_2\cdot CMeR\cdot CH(CN)\cdot CO\cdot NH_2$ $\qquad$ $R\cdot CO\cdot CH_2\cdot CMeR\cdot CH_2\cdot CO_2H$ (XII.)

The reduction of the keto-acids, made by the foregoing methods, was usually effected by Clemmensen's method, but in certain cases no reduction occurred in 100 hours, even with the addition of toluene (Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1938). The Wolff–Kishner method and reduction by sodium and alcohol were unsuccessful in the few cases tried and a generally applicable process is still to be found; pressure hydrogenation offers the best prospects. In case *sec.*-alcohols were obtained we studied the reduction of di-*n*-decylcarbinol as a model. With hydriodic acid and phosphorus at 130° it gave the corresponding iodide, which was reduced to heneicosane, m. p. 42°, by zinc dust and alcohol.

A few preliminary experiments were made on the use of methods depending on migration of groups.

Tiffeneau and Lévy (*Bull. Soc. chim.*, 1931, **49**, 1628, 1690), basing their conclusions on the work of Meerwein (*Annalen*, 1913, **396**, 256; 1919, **419**, 121), Parry (J., 1915, **107**, 108), and Nybergh (*Ber.*, 1922, **55**, 1960), have pointed out that in pinacols of the type $CR_2(OH)\cdot CMe_2\cdot OH$ it is the longer chain alkyl group that possesses the greater migratory aptitude and as the chain in R grows longer the proportion of the pinacolone, $R\cdot CO\cdot CMe_2R$, in the product increases.

The pinacol from ethyl α-hydroxy*iso*butyrate and *n*-amylmagnesium bromide was converted through the pinacolone into 2 : 2-dimethylheptoic acid, isolated as the amide, but the investigation was abandoned when it was found that interaction of *n*-heptylmagnesium bromide and *n*-decylmagnesium bromide with ethyl α-hydroxy*iso*butyrate afforded no *as*-pinacols but only hydrocarbons. Moreover we were unable to obtain any significant yield of pinacol by reduction of methyl *n*-decyl ketone.

Haller and Lassieur (*Compt. rend.*, 1910, **150**, 1017) obtained a compound, $C_{22}H_{44}O$, by Sabatier–Senderens reduction of methyl *n*-nonyl ketone. They formulated this as a pinacolone, $C_9H_{19}\cdot CO\cdot CMe_2\cdot C_9H_{19}$. It seems much more probable that it is derived by reduction of a self-condensation product and is $C_9H_{19}\cdot CHMe\cdot CH_2\cdot CO\cdot C_9H_{19}$.

Experimental.

2 : 2-*Dimethyl-lauric Acid.*—A mixture of ωω-dimethyl-ω-*n*-decylacetophenone (Haller, *loc. cit.*), twice its volume of toluene, and powdered sodamide (2 mols.) was refluxed for 6 hours. The amide was isolated (pearly plates; yield, 48%), dissolved in 10 times its weight of sulphuric acid, and sodium nitrite (1·25 mols.) gradually added. After 12 hours, the mixture was heated on the steam-bath for ½ hour. The product, b. p. 165—180°/10 mm., melted indefinitely at about 30° (Haller, *loc. cit.*, ascribes the m. p. 27° to the dimethyl-lauric acid). This material contained nitrogen and was clearly a mixture of the acid and the amide. It was esterified by means of boiling alcoholic sulphuric acid; the ester was a colourless oil, b. p. 145—150°/10 mm., with a pineapple odour. On hydrolysis the pure acid, b. p. 175—180°/10 mm., m. p. 4°, was obtained (Found: C, 73·5; H, 12·1. Calc. for $C_{14}H_{28}O_2$: C, 73·7; H, 12·3%).

2 : 2-*Dimethylstearic Acid.*—A mixture of stearoylbenzene (10 g.), powdered sodamide (1·3 g.), and toluene (15 c.c.) was refluxed for ½ hour, methyl iodide (5 c.c.) added, and boiling continued for 2 hours. Water was added, and the organic layer separated, dried, and distilled until a little toluene had been collected. When the water had been completely removed, the volume was made up to 25 c.c. by the addition of toluene, sodamide (3 g.) was added, and the liquid refluxed for 3 hours. On pouring into water, pearly plates (2 g.) separated from the toluene layer. These were recrystallised from light petroleum (b. p. 40—60°) and had m. p. 81°. This amide was converted into the *acid* by prolonged treatment with sulphuric acid and sodium nitrite; b. p. 215—220°/15 mm., m. p. 42° (Found: C, 76·6; H, 12·9. $C_{20}H_{40}O_2$ requires C, 76·9; H, 12·8%).

The liquid (4 g.) remaining in the toluene was isolated and treated with sodium nitrite and sulphuric acid. The products were benzoic acid (from incompletely methylated material, see below) and crude dimethylstearic acid. This gave 0·5 g. of pure distilled ester, which was saponified to the acid, m. p. 42°.

*ωω-Di-*n*-decylacetophenone.*—Ethyl di-*n*-decylmalonate, b. p. 264—268°/10 mm., was obtained in 75% yield from ethyl malonate (20 g.), *n*-decyl bromide (57 g.), sodium (2·9 g.), a little sodium iodide, and alcohol (50 c.c.), the mixture being refluxed for 6 hours. On hydrolysis with aqueous alcoholic sodium hydroxide it gave di-*n*-decylmalonic acid, greasy plates, m. p. 60—61°, in almost quantitative yield, and this decomposed at 185° to 2-*n*-decyl-lauric acid, m. p. 54° after crystallisation from acetone. The acid (28 g.) and thionyl chloride (50 c.c.) were allowed to react at 60° for 5 hours; the resulting 2-*n*-decyl-lauryl chloride (22 g., b. p. 245—250°/10 mm.) furnished the amide, colourless needles, m. p. 115—116°, from alcohol, on treatment with aqueous ammonia. The chloride (21 g.) was added to a mixture of benzene (100 c.c.) and powdered aluminium chloride (8·8 g.). After 12 hours the mixture was heated at 40° for 3 hours and then decomposed by ice. *Di-*n*-decylacetophenone* was obtained as a pale yellow oil (13 g.), b. p. 275—280° (Found: C, 83·0; H, 12·6. $C_{28}H_{48}O$ requires C, 83·2; H, 12·6%). It could not be converted into a crystalline oxime, semicarbazone, or dinitrophenylhydrazone.

When it was treated with sodamide in boiling toluene, ammonia was evolved, but subsequent attempted methylation with methyl iodide under the usual conditions was unsuccessful. After decomposition of the product with sodamide, oils, b. p. 170—280°/10 mm., were isolated, but there was no evidence of the presence of a trisubstituted acetamide. When the initial product was treated with sulphuric acid and sodium nitrite, benzoic acid was produced. *iso*Butyrophenone was found to be decomposed with formation of benzoic acid under the same conditions, whereas phenyl *tert.*-butyl ketone was not changed (cf. Lapworth and Steele, J., 1911, **99**, 1886). Similar experiments were carried out with *ωω*-di-*n*-heptylacetophenone. 2-*n*-Heptylnonoic acid (b. p. 190—195°/12 mm.) (Stanley, Jay, and Adams, *J. Amer. Chem. Soc.*, 1929, **51**, 1261) with thionyl chloride furnished the chloride, b. p. 170—175°, in 80% yield. Condensation with benzene in presence of aluminium chloride afforded diheptylacetophenone, b. p. 210—215°/15 mm. This ketone could not be methylated by means of sodamide and methyl iodide. The crude product was decomposed by sodium nitrite and sulphuric acid to benzoic acid and a small quantity of a neutral compound, m. p. 44°. The use of *iso*amyl nitrite and alcoholic sodium ethoxide (Lapworth and Steele, *loc. cit.*) gave ethyl benzoate and the substance, m. p. 44°, which is probably di-*n*-heptyl ketone.

2-n-*Octylundecamide.*—Sodamide (8 g.) was added during 15 minutes to a mixture of undeconitrile (33 g., b. p. 145°/14 mm., from undecamide by the action of thionyl chloride), *n*-octyl bromide (39 g.), and benzene (50 c.c.). After 1 hour the whole was refluxed for 1 hour. The product was a colourless oil (15 g.), b. p. 215—220°/12 mm. This 2-*n*-octylundeconitrile could not be methylated by means of sodamide and methyl iodide. When refluxed with a mixture of acetic acid, sulphuric acid and water (4 : 2 : 1), it afforded the *amide*, m. p. 109°, from alcohol (Found: N, 4·9. $C_{19}H_{39}ON$ requires N, 4·7%). The action of syrupy phosphoric acid on the nitrile at 160° (cf. Berger and Olivier, *Rec. Trav. chim.*, 1927, **46**, 600) also gave the amide.

2-*Methyl*-2-n-*decyl-lauronitrile.*—Powdered sodamide (3·9 g.) was added to propionitrile (5·5 g.) and *n*-decyl bromide (22 g.) in toluene (20 c.c.), and the mixture kept for 15 minutes and then heated on the steam-bath for 2 hours. The product was isolated, and substances, b. p. <140°/14 mm., rejected. The residue was re-treated as above with sodamide, and decyl bromide in toluene, the mixture being refluxed for 5 hours. On working up, a small quantity of a low-melting base was obtained and the main product (12 g.) was a colourless, odourless oil, b. p. 230—245°/1 mm. (Found: N, 4·4. $C_{23}H_{45}N$ requires N, 4·2%). This *nitrile* was unchanged by a boiling mixture of acetic and sulphuric acids or by heating for 5 hours at 160° with syrupy phosphoric acid fortified by addition of a little phosphoric anhydride.

4-*αα-Dimethylundecylveratrole.*—1 : 1-Dimethylundecan-1-ol (35 g., b. p. 135—138°/13 mm., from 50 g. of ethyl undecoate, 75 g. of methyl iodide and 6·5 g. of magnesium) was heated with thionyl chloride (40 c.c.) at 40° for an hour. The excess of the reagent was removed under diminished pressure, and the product washed with aqueous sodium carbonate and dried. It was not distilled because it suffered some decomposition at 90°. A mixture of this dimethylundecyl chloride (25 g.), veratrole (16 g.), carbon disulphide (60 c.c.), and powdered aluminium chloride (20 g.) was stirred for 3 hours. After 4 days the *product* (18 g.) was isolated in the known manner and was obtained as a pale yellow oil, b. p. 220—225°/13 mm. (Found: C, 78·9; H, 11·4. $C_{21}H_{36}O_2$ requires C, 78·7; H, 11·2%). The corresponding dimethylundecylcatechol, b. p. 240—245°/13 mm., was prepared by refluxing the dimethyl ether (18 g.) with hydrobromic acid (40 c.c., *d* 1·5) and acetic acid (40 c.c.) for 4 hours. The pale yellow oil darkened on keeping and gave an olive-green coloration with alcoholic ferric chloride. Powdered potassium permanganate (25 g.) was added during 2 hours to a well-stirred solution of this catechol derivative (8 g.) in acetone (250 c.c.); the mixture was then refluxed for 1 hour. The isolated product did not appear to have been completely oxidised and it was accordingly dissolved in dilute aqueous sodium hydroxide and oxidised at 50° by the addition of 5% aqueous potassium permanganate until the colour of the latter persisted. The product was isolated, dissolved in aqueous sodium hydroxide (30 c.c. of 5%), hydrogen peroxide (15 c.c. of 10%) added, and the solution was kept for 12 hours. The isolated acid (2·2 g.) had b. p. 175—180°/12 mm.; a considerable residue indicated that oxidation was incomplete even after the above treatment. The acid was identified as 2 : 2-dimethyl-lauric acid (above) by conversion into the amide, m. p. 94°.

The method of Reichstein (*loc. cit.*) was also tried and a small yield of ethyl 1′ : 1′-dimethylundecylfuroate, b. p. 220—235°/12 mm., obtained. On oxidation this furnished some dimethyl-lauric acid (amide, m. p. 90°), but the process was not satisfactory.

1-*Methyl*-1-*heptyloctan*-1-*ol* (32 g., b. p. 165°/13 mm.) was obtained from ethyl acetate (20 g.), *n*-heptyl bromide (80 g.), and magnesium (5·5 g.) (Found: C, 79·5; H, 13·9. $C_{16}H_{34}O$ requires C, 79·3; H, 14·0%). The product of the condensation of the corresponding chloride with veratrole in the presence of aluminium chloride had b. p. 150—250° and could not be separated into definite fractions.

1-*Methyl*-1-n-*octyldecoic Acid.*—1-Methyl-1-*n*-octylnonan-1-ol (10 g., b. p. 190—195°/20 mm., m. p. −5°) was obtained from ethyl acetate (10 g.), *n*-octyl bromide (48 g.), and magnesium (6 g.). It was converted into the chloride by reaction with thionyl chloride. A mixture of methyloctylnonyl chloride (29 g.), methyl furoate (12·5 g.), carbon disulphide (60 c.c.), and powdered aluminium chloride (40 g.) was kept for a week and then worked up in the known manner. The material (0·8 g.), b. p. 200—260°, was redistilled, b. p. 235—260°/13 mm. (0·5 g.). The viscous acid obtained on hydrolysis could not be crystallised; it was oxidised in dilute aqueous sodium hydroxide with potassium permanganate at 35° until the oxidising agent was no longer reduced. The acidic product (0·2 g.) was a viscous oil, b. p. 220—235°/12 mm. (Found: C, 74·4; H, 13·8. $C_{18}H_{36}O_2$ requires C, 74·7; H, 13·6%).

1-Ethyl-1-*n*-octylnonan-1-ol (10 g., b. p. 190—195°, m. p. −10°, from 15 g. of ethyl propionate, 48 g. of *n*-octyl bromide, and 6 g. of magnesium) and 1-methyl-1-*n*-decylundecan-1-ol (11 g., b. p. 225—230°/12 mm., m. p. 21°, from 5 g. of ethyl acetate, 25 g. of *n*-decyl bromide, and 2·7 g. of magnesium) were converted into chlorides, but no recognisable products were obtained on attempted condensation with methyl furoate and subsequent oxidation.

Attempted Reduction of Ethyl 2-n-*Nonyl-2-acetoundecoate.*—The ester (b. p. 240°/18 mm.) was treated with amalgamated zinc in boiling alcoholic hydrogen chloride solution, with sodium in boiling alcohol, and with hydrogen in glacial acetic acid solution at 50° in the presence of Adams's catalyst. In no case did reduction occur and the products on hydrolysis furnished only 2-*n*-nonylundecoic acid, m. p. 45°, and dinonylacetone.

Ethyl 5-Keto-6-acetyl-6-carbethoxy-3 : 3-dimethylundecoate.—A solution of *ββ*-dimethylglutaric anhydride (10 g.) in alcohol (20 c.c.) was refluxed for 30 hours, and the solvent evaporated under diminished pressure. A mixture of the

viscous half-ester with thionyl chloride (12 c.c.) was kept for 2 hours and then heated at 45° for 30 minutes. The product distilled as a colourless oil (9·2 g.), b. p. 110°/10 mm. The whole of this ester chloride was added to ethyl sodio-2-acetylheptoate (from 12 g. of the ester, b. p. 121°/10 mm., and 1·05 g. of sodium) in ether (25 c.c.). After the initial reaction, the mixture was refluxed for 15 minutes; the *product* was a colourless oil (6·5 g.), b. p. 200°/10 mm., with a faint pleasant odour (Found: C, 64·9; H, 9·3. $C_{19}H_{32}O_6$ requires C, 64·0; H, 9·2%).

5-Keto-3 : 3-dimethylundecoic Acid.—The above ester (5 g.) was shaken with an excess of aqueous sodium hydroxide (5%) for 15 hours and then acidified; the product, collected by means of ether, was refluxed for 15 hours with 5% sulphuric acid, again isolated, and refluxed for 10 hours with 10% aqueous sodium hydroxide. After steam distillation to remove methyl hexyl ketone, the acid was liberated and isolated (0·25 g.), b. p. 190°/10 mm. It formed a 2 : 4-*dinitrophenylhydrazone*, which crystallised from alcohol in bright orange needles, m. p. 122° (Found: N, 13·2. $C_{19}H_{28}O_6N_2$ requires N, 13·7%). Reduction by Clemmensen's method gave a colourless, viscous oil that did not react with dinitrophenylhydrazine, but the yield of the keto-acid was so unfavourable that the subject was not pursued further.

3 : 3-*Dimethyltetradecoic Acid.*—4-Carbethoxy-3 : 3-dimethylbutyryl chloride (55 g.) reacted with ethyl sodio-2-acetyldecoate (from 66 g. of the ester and 6·2 g. of sodium) to form ethyl 5-keto-6-acetyl-6-carbethoxy-3 : 3-dimethyltetradecoate (80 g.), b. p. 240—242°/9 mm. Half of this material was hydrolysed by treatment with ammonia in dry ether (cf. Bardhan, J., 1936, 1850) and subsequently with boiling 12% aqueous sodium hydroxide. The resulting acid was esterified and the yield of pure keto-ester (see below) was 6 g. The other half (40 g.) was shaken with aqueous sodium hydroxide (500 c.c. of 2·5%) for 40 hours; sodium hydroxide (20 g.) was then added, and the solution refluxed for 20 hours. The acid was then isolated and refluxed with 15% sodium hydroxide solution for 3 hours; it was again isolated and esterified by means of boiling 5% alcoholic sulphuric acid. Ethyl 5-keto-3 : 3-dimethyltetradecoic acid (9 g.), b. p. 186—188°/9 mm., was obtained. The corresponding acid is a low-melting solid; 2 : 4-dinitrophenylhydrazone, m. p. 85°. It was refluxed for 100 hours with 20% hydrochloric acid and amalgamated zinc; the reduced *acid* had b. p. 195°/10 mm., m p. 15° (Found: C, 74·8; H, 12·3. $C_{14}H_{32}O_2$ requires C, 75·0; H, 12·5%).

5-Keto-3-methyl-3-n-hexylnonoic Acid.—The solid that separated during 3 days from a mixture of methyl hexyl ketone (40 g.), ethyl cyanoacetate (90 g.), and saturated alcoholic ammonia (100 c.c.) was collected and treated with dilute hydrochloric acid. The resulting *aa'*-dicyano-*β*-methyl-*β*-hexylglutarimide (cf. Guareschi and Grande, *Atti R. Accad. Sci. Torino*, 1900, **34**, 18) was refluxed with sulphuric acid (100 c.c.), acetic acid (70 c.c.), and water (30 c.c.) for 8 hours. The methylhexylglutaric acid was collected by thorough extraction of the diluted mixture with ether and then esterified by boiling 10% alcoholic sulphuric acid; the ester (35 g.) was a pleasant smelling oil, b. p. 163—165°/9 mm. On hydrolysis the pure *β-methyl-β-n-hexylglutaric acid* was obtained; it crystallised from light petroleum in colourless prisms, m. p. 61° (Found: C, 62·5; H, 9·5. $C_{13}H_{24}O_4$ requires C, 62·6; H, 9·5%).

The acid was converted into its anhydride by boiling with acetic anhydride, and the mixture distilled. Methylhexylglutaric anhydride was obtained as a colourless oil, b. p. 196°/9 mm. It was converted into the semi-ester by means of slightly more than the theoretical amount of sodium ethoxide in the minimum quantity of anhydrous alcohol. The oily acid ester was isolated, dried, and mixed with an equal volume of thionyl chloride; after 3 hours the mixture was heated at 45° for 1 hour. The ester chloride had b. p. 167°/9 mm. (76% yield from the acid).

(i) After 4-carbethoxy-3-methyl-3-*n*-hexylbutyryl chloride (15 g.) had been added to ethyl sodio-2-acetylvalerate (13·5 g. of the ester and 1·9 g. of sodium) in ether (30 c.c.), the mixture was refluxed for 3 hours. Ethyl 5-keto-6-acetyl-6-carbethoxy-3-methyl-3-*n*-hexylnonoate (18 g., b. p. 200°/10 mm.) was obtained on distillation of the product.

This ester was hydrolysed by following, exactly, the second of the methods mentioned above in the section "3 : 3-dimethyltetradecoic acid." The crude acidic product was dissolved in light petroleum, and the solution washed with very dilute aqueous potassium carbonate. This removed methylhexylglutaric acid, which was recovered by acidification of the washings. The residue (0·6 g., b. p. 190—210°/14 mm.) in the organic solvent was esterified with methyl-alcoholic hydrogen chloride and distillation of the ester gave two fractions, b. p. 160—165°/10 mm. and 178—182°/10 mm. The former was shown by hydrolysis to be methyl methylhexylglutarate and the latter was mainly the required *keto-ester* (Found: C, 70·6; H, 11·0. $C_{17}H_{32}O_3$ requires C, 71·7; H, 11·2%). Owing to the small quantity (0·3 g.) available the specimen could not be freed from the lower-boiling ester ($C_{14}H_{26}O_4$ requires C, 65·1; H, 10·1%).

(ii) The above ester chloride (30 g.) was added to a solution of zinc di-*n*-butyl (9 g.) (Organic Syntheses, XII, 89) in benzene (30 c.c.), and the solution refluxed for 1 hour. On working up, a crude oil, b. p. 195—210°/9 mm., was obtained and its methyl ester, b. p. 178—182°/9 mm., was separated from some admixed methyl methylhexylglutarate, b. p. 163—168°/9 mm. The recovered keto-acid had b. p. 205—210°/9 mm. and formed a red, oily 2 : 4-dinitrophenylhydrazone.

5-Keto-3-methyl-3-n-octylundecoic Acid.—A mixture of methyl *n*-octyl ketone (50 g.), ethyl cyanoacetate (112 g.), and saturated alcoholic ammonia (200 c.c.) deposited in a few days *aa'-dicyano-β-methyl-β-octylglutarimide* (55 g.), which crystallised from light petroleum in pearly plates, m. p. 139° (Found: N, 14·8. $C_{16}H_{28}O_2N_2$ requires N, 14·5%). On refluxing with 50% sulphuric acid for 4 hours, practically pure *β-methyl-β-n-octylglutarimide* was obtained. This separated from light petroleum in plates, m. p. 91° (Found: N, 6·1. $C_{14}H_{25}O_2N$ requires N, 5·9%). The imide was hydrolysed by refluxing for 6 hours with a mixture (10 : 7 : 3) of sulphuric acid, acetic acid, and water. The crude oily acid was esterified with 10% alcoholic sulphuric acid (ester, b. p. 195°/18 mm.) and hydrolysis then afforded methyloctylglutaric acid as an oil that solidified in prisms, m. p. 58°. This was converted into the anhydride by refluxing with acetic anhydride (50 c.c.); the product (31 g.) was a colourless, viscous oil, b. p. 210—212°/13 mm.

The ester chloride (20 g., b. p. 185—187°/9 mm.) was prepared from the anhydride (18 g.) as in the analogous examples. Successive treatment with aqueous ammonia, aqueous sodium hydroxide and hydrochloric acid regenerated the imide, m. p. 91°.

Following the usual procedure, the ester chloride (14 g.) and ethyl sodio-2-acetylheptoate (12 g. of the ester; reaction mixture refluxed for 2 hours) afforded ethyl 5-keto-6-acetyl-6-carbethoxy-3-methyl-3-*n*-octylundecoate (15 g.) as a colourless, viscous oil, b. p. 255—265°/10 mm. This was shaken for 30 hours with aqueous sodium hydroxide (350 c.c. of 5%) and for 10 hours more after the addition of sodium hydroxide (15 g.) and alcohol (200 c.c.). The solution was then refluxed for 8 hours, and the acids liberated and isolated by means of ether. Analysis of the oil (8 g., b. p. 210—230°/10 mm.) obtained on distillation showed it to be a mixture. It was dissolved in light petroleum, and methyloctylglutaric acid (recovered, m. p. 58°) removed by washing with dilute aqueous potassium carbonate. The light petroleum solution was shaken with dilute hydrochloric acid and distilled. The *keto-acid* (1·0 g.) had b. p. 235—240°/10 mm. (Found: C, 73·2; H, 11·6. $C_{20}H_{38}O_3$ requires C, 73·6; H, 11·6%). The substance gave no crystalline semicarbazone and a red, oily 2 : 4-dinitrophenylhydrazone. On reduction by Clemmensen's method (refluxing for 100 hours), 3-methyl-3-*n*-octylundecoic acid, b. p. 225—230°/20 mm., was obtained; it did not react with 2 : 4-dinitrophenylhydrazine.

n-*Decyl Methyl and Ethyl Ketones.*—These ketones were conveniently prepared on a small scale by the action of undecoyl chloride on methylzinc iodide and ethylzinc iodide respectively, under the known conditions (toluene as solvent). On a larger scale the method of Pickard and Kenyon (J., 1911, **99**, 57) was adopted. Methyl *n*-decyl ketone (b. p. 245°, m. p. 20°) gives a 2 : 4-dinitrophenylhydrazone, m. p. 81°, and a semicarbazone, m. p. 125° (Pickard and Kenyon give

122—123°; Stoll, Ruzicka, and Schinz, *Helv. Chim. Acta*, 1928, **11**, 670, give 104—105°, which is probably a misprint). Ethyl *n*-decyl ketone, m. p. 31° (Pickard and Kenyon, 25°), forms a 2 : 4-dinitrophenylhydrazone, m. p. 55°, and a semicarbazone, m. p. 93° (lit., 90°). This ketone was also obtained in poor yield from the product of reaction of ethylmagnesium bromide and undeconitrile.

αα'-Dicyano-β-methyl-β-n-decylglutarimide.—A mixture of methyl decyl ketone (12 g.), ethyl cyanoacetate (15 g.), and saturated alcoholic ammonia (50 c.c.) gradually deposited the condensation *product*. It crystallised from light petroleum in pearly plates, m. p. 135° (Found : N, 13·2. $C_{18}H_{27}O_2N_3$ requires N, 13·2%). Methyl-*n*-decylglutaric anhydride (9 g.), b. p. 235—237°/18 mm., was obtained in the usual manner and on hydration gave the acid, colourless prisms, m. p. 63—64°. The anhydride prepared from the pure acid had m. p. 31°. The imide, obtained by heating the anhydride with urea and crystallised from light petroleum, had m. p. 71°.

Ethyl *n*-decyl ketone did not undergo the Guareschi reaction; it could be condensed neither with cyanoacetamide under various conditions nor with ethyl cyanoacetate in the presence of sodium ethoxide or piperidine.

α-Methyl-α-n-decylsuccinic Anhydride.—A mixture of methyl decyl ketone (92 g.), ethyl cyanoacetate (60 g.), toluene (200 c.c.), and piperidine (3 c.c.) was refluxed under a condensing system that included a water-trap. The formation of water ceased after 3 hours and, on distillation, ethyl 2-cyano-3-methyl-Δ^2-tridecenoate was obtained as a colourless oil (120 g.), b. p. 196—200°/16 mm. [A mixture of this ester (5 g.), ethyl cyanoacetate (2 g.), and saturated alcoholic ammonia (20 c.c.), kept for 8 hours, deposited 4 g. of *αα'*-dicyano-*β*-methyl-*β*-*n*-decylglutarimide (above), m. p. 135° after crystallisation from light petroleum.] A solution of sodium cyanide (25 g.) in the minimum quantity of water and enough alcohol to give a clear solution were added, the temperature rising. After 1 hour an equal volume of water was added, and the solution acidified. The ethyl 2 : 3-dicyano-3-methyltridecoate was collected by means of ether. It decomposed to some extent on distillation (b. p. 214—220°/15 mm.) and was used in the crude form for the next stage, which was effected by refluxing for 4 hours with sulphuric acid (100 c.c.), acetic acid (70 c.c.), and water (30 c.c.). [Refluxing with 50% sulphuric acid for 2 hours carried the hydrolysis as far as the imide.] The acid was collected by ether and esterified by boiling alcoholic sulphuric acid (150 c.c. of 10%); the ethyl *α*-methyl-*α*-*n*-decylsuccinate was a colourless oil (81 g.), b. p. 189—192°/8 mm. The acid obtained on hydrolysis was a viscous oil; it was converted by boiling acetic anhydride into the *anhydride*, b. p. 187°/8 mm., m. p. 37° (Found : C, 70·9; H, 10·3. $C_{18}H_{32}O_3$ requires C, 70·9; H, 10·2%). The ester (48 g.) was refluxed for 20 minutes with an alcoholic solution of sodium ethoxide (4·5 g. of sodium), water (5 c.c.) being gradually added. After the addition of acetic acid (5 c.c.) most of the alcohol was evaporated under diminished pressure. The residue was taken up in 3% sodium hydroxide solution (500 c.c.), the undissolved oil removed, and the acid set free and collected by means of ether. A mixture with thionyl chloride (50 c.c.) was kept for 8 hours, heated at 45° for 1 hour, and distilled. 3-Carbethoxy-3-methyltridecoyl chloride (31 g.), b. p. 160°/1 mm., was thus obtained. Successive treatment with aqueous ammonia, aqueous sodium hydroxide, and hydrochloric acid gave the *imide*, m. p. 98° (Found : C, 71·0; H, 10·8; N, 5·4. $C_{18}H_{27}O_2N$ requires C, 71·2; H, 10·7; N, 5·5%).

α-Methyl-α-hexylsuccinic acid derivatives were made in a similar way. Methyl *n*-hexyl ketone (100 g.), ethyl cyanoacetate (70 g.), and piperidine (1·5 g.), condensed in boiling toluene, gave ethyl 2-cyano-3-methyl-Δ^2-nonenoate (yield, 80%), b. p. 162—168°/14 mm. Ethyl methylhexylsuccinate, obtained by addition of hydrogen cyanide and hydrolysis of the product, had b. p. 155—158°/14 mm.; the anhydride of the corresponding acid had b. p. 160—162°/14 mm. The imide, prepared by partial hydrolysis of the dicyano-ester or by heating the anhydride with urea, crystallised from ethyl acetate–light petroleum in plates, m. p. 115°. The ethyl ester chloride had b. p. 153—155°/13 mm. Hydrolysis of the condensation product of this ester chloride with ethyl sodio-2-acetylvalerate or of the ester chloride of methyldecylsuccinic acid with ethyl sodio-2-acetylheptoate gave no new keto-acids and the starting products (acids) were regenerated.

Methyl 5-Keto-3-methyl-3-n-octyl-laurate.—A solution of fused zinc chloride (20 g.) in ether (40 c.c.) and then toluene (100 c.c.) were added to a Grignard reagent prepared from *n*-heptyl bromide (16·5 g.), magnesium (2·2 g.), and ether (50 c.c.). The liquid was distilled until the thermometer registered 108° and toluene (40 c.c.) was introduced during this process. 4-Carbethoxy-3-methyl-3-*n*-octylbutyryl chloride (21 g.) was added to the cooled solution, which was then heated on the steam-bath for 3 hours with occasional stirring. The product (13 g.) was a colourless, viscous oil, b. p. 230—240°/20 mm. It was hydrolysed by means of alcoholic potassium hydroxide, whereby some heptyl alcohol and some of the methyloctylglutaric acid were formed. The isolated acid was converted into its *methyl* ester (9 g.), b. p. 235°/19 mm. (Found : C, 74·2; H, 11·6. $C_{32}H_{62}O_3$ requires C, 74·6; H, 11·8%.) In a similar experiment with *n*-octyl bromide on the one hand and methyldecylsuccinic anhydride on the other, the formation of a new keto-acid did not occur. The higher-boiling product consisted entirely of unchanged anhydride, b. p. 187°/8 mm., m. p. 37°.

2-Keto-1 : 3-dimethyl-3 : 5-di-n-decyl-2 : 3-dihydropyrrole.—α-Methyl-α-*n*-decylsuccinic anhydride (20 g.) was heated with aqueous methylamine (6·5 c.c. of 33%), and the mixture distilled; the methylimide was a colourless, viscous oil, b. p. 205°/15 mm. It was mixed with a Grignard solution prepared from *n*-decyl bromide (35 g.), magnesium (4 g.), and ether (60 c.c.) and heated on the steam-bath for 2 hours. On working up, a very viscous oil (8 g.), b. p. 265—280°/15 mm. (Found : N, 3·6. $C_{36}H_{69}ON$ requires N, 3·6%), was obtained, along with eicosane and unchanged methylimide in the lower-boiling fractions. The *substance* resisted the action of boiling hydrobromic acid during 10 hours and other attempted methods of hydrolysis gave unchanged material, tar, or both.

5-Keto-3 : 3-dimethyl-lauric Acid.—A Grignard solution prepared from *n*-heptyl bromide (40 g.) and magnesium (5 g.) in ether (90 c.c.) was gradually added with stirring to *ββ*-dimethylglutaromethylimide (22 g.) dissolved in warm benzene (50 c.c.); a white precipitate at once formed. After refluxing for 3 hours, the product was isolated, b. p. 195—206°/16 mm. It was hydrolysed during 10 hours by a boiling mixture of sulphuric acid (20 c.c.), acetic acid (60 c.c.), and water (25 c.c.). The acid was isolated and esterified with ethyl alcohol, and the ester distilled (7 g.), b. p. 179—181°/14 mm. Hydrolysis afforded the pure acid, b. p. 203°/18 mm. The semicarbazone separated from methyl alcohol in prisms, m. p. 113°, and the 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol in vermilion needles, m. p. 99° (Found : N, 12·9. $C_{29}H_{30}O_6N_4$ requires N, 13·2%).

1-β-Ketononylcyclohexane-1-acetic Acid.—cyclo*Hexane*-1 : 1-*diacetomethylimide* was prepared by distilling a solution of its methylammonium salt (1MeNH$_2$ suffices). It had b. p. 184°/15 mm. and crystallised from alcohol in prisms, m. p. 66° (Found : N, 7·4. $C_{11}H_{15}O_2N$ requires N, 7·3%). A solution of this methylimide (30 g.) in benzene (100 c.c.) was added, all at once, to the Grignard reagent prepared from *n*-heptyl bromide (30 g.) and magnesium (6 g.) in ether (100 c.c.). After 12 hours, the mixture was refluxed for 1 hour. The product (6 g.), b. p. 215—225°/15 mm., was obtained after a considerable amount of the unchanged material had been recovered. It was refluxed for 16 hours with hydrobromic acid (*d* 1·15), and the acid isolated and esterified. Distillation of the ester gave a fraction, b. p. 160—175°/15 mm., largely ethyl *cyclo*hexanediacetate, a fraction, b. p. 175—200°/15 mm., and material of higher b. p., possibly containing still some unchanged methylimide. Hydrolysis of the middle fraction gave an oily *acid* which partly crystallised (0·4 g., m. p. 151°) (Found : C, 72·8; H, 10·7. $C_{17}H_{30}O_3$ requires C, 72·3; H, 10·6%).

Ethyl 3-Methyl-3-(β-cyclohexylethyl)nonoate.—A mixture of *β*-methyl-*β*-*n*-hexylglutaric anhydride (10 g.), benzene (20 c.c.), and powdered aluminium chloride (15 g.) was kept for 6 hours. The product was isolated as a viscous oil, b. p. 225—230°/10 mm. It gave a red, oily 2 : 4-dinitrophenylhydrazone, but no crystalline semicarbazone or oxime

could be obtained. The ethyl ester (10 g.), b. p. 214—216°/12 mm. (ethyl 4-benzoyl-3-methyl-3-*n*-hexylbutyrate), was dissolved in an equal volume of alcohol and hydrogenated at 200°/50—60 atms. in the presence of Raney nickel. The reduced *ester*, b. p. 190—200°/14 mm. (Found: C, 77·5; H, 11·1. $C_{20}H_{38}O_2$ requires C, 77·4; H, 12·3%), furnished, on hydrolysis, the acid, b. p. 225—228°/13 mm.

2-Phenacyl-2-methyl-lauric Acid.—A mixture of α-methyl-α-*n*-decylsuccinic anhydride (10 g.), benzene (20 c.c.), and powdered aluminium chloride (15 g.) was kept for 20 hours and then heated at 40° for 1 hour. The *product*, collected by means of ether, solidified; it crystallised from light petroleum in colourless prisms (10 g.), m. p. 87° (Found: C, 75·5; H, 9·8. $C_{21}H_{32}O_3$ requires C, 75·9; H, 9·6%). Search for an isomeric product was fruitless and it is evident that the reaction proceeded almost exclusively in one of the two possible directions. It has been established in several similar cases that it is the α-substituted, sterically hindered carboxyl group that survives.

Ethyl 2-Methyl-2-(β-cyclohexylethyl)laurate.—A mixture of the above acid (8 g.), alcohol (15 c.c.), and Raney nickel (*ca.* 5 g.) was shaken under hydrogen at 200°/50 atms. The product was esterified and distilled (6 g.), b. p. 245—250°/14 mm. (Found: C, 78·9; H, 12·4. $C_{33}H_{64}O_3$ requires C, 78·4; H, 12·5%).

Prolonged reduction of the keto-acid (5 g.) according to Clemmensen (using 50 g. of amalgamated zinc) gave a product, b. p. 240—280°/9 mm. This material still contained some keto-acid and was obviously a mixture. On trituration with light petroleum, it partly solidified, and by fractional crystallisation from ethyl acetate–light petroleum two substances were separated, namely, *γ-phenyl-α-methyl-α-n-decylbutyrolactone-A*, m. p. 102° (Found: C, 79·4; H, 10·2. $C_{21}H_{32}O_2$ requires C, 79·6; H, 10·1%), and the more sparingly soluble *isomeride-B*, m. p. 164° (Found: C, 79·6; H, 10·1%). The substances showed the typical behaviour of lactones and are doubtless the *r*- and the *meso*-modification produced by the presence of two asymmetric carbon atoms in the molecule.

2-Phenacyl-2-methyloctoic Acid.—(i) A mixture of α-methyl-α-*n*-hexylsuccinic anhydride (10 g.), benzene (30 c.c.), and powdered aluminium chloride (18 g.) was kept for 10 hours and decomposed with ice. Evaporation of the benzene left a crystalline residue. The *substance* crystallised from ethyl acetate–light petroleum in prisms (9 g.), m. p. 95° (Found: C, 73·6; H, 8·8. $C_{17}H_{24}O_3$ requires C, 73·9; H, 8·7%).

(ii) A mixture of 3-carbethoxy-3-methylnonoyl chloride (5 g.), benzene (15 c.c.), and powdered aluminium chloride (9 g.) was kept for 12 hours. The oily product was isolated and hydrolysed by means of 20% aqueous sodium hydroxide; the liberated acid crystallised from ethyl acetate–light petroleum in prisms (3·5 g.), m. p. 95° alone or mixed with the product of (i).

n-*Amyl β-n-Amylisopropenyl Ketone.*—Methylaniline (35 g.) in benzene (100 c.c.) was added to a Grignard solution prepared from ethyl bromide (50 g.), magnesium (9 g.), and ether (120 c.c.), and the solution gradually added with stirring to methyl *n*-amyl ketone (75 g.) in benzene (50 c.c.). After 10 hours, dilute hydrochloric acid was added, and the *product* isolated as a pale yellow oil (55 g.), b. p. 140°/13 mm. (Found: C, 80·1; H, 12·5. $C_{14}H_{26}O$ requires C, 80·0; H, 12·4%). Oxidation with alkaline permanganate afforded methyl amyl ketone and *n*-hexoic acid.

Ethyl 5-Keto-3-methyl-3-n-amyldecoate.—(i) A mixture of amyl amyl*iso*propenyl ketone (20 g.), ethyl malonate (16 g.), and alcoholic sodium ethoxide (2·3 g. of sodium in 35 c.c.) was refluxed for 1 hour. Potassium hydroxide (10 g.) and water (30 c.c.) were added, and refluxing continued for 2 hours. Acidification precipitated *5-methyl-2-butyl-5-n-amylcyclohexane-1 : 3-dione* (15 g.). This crystallised from acetone in colourless needles, m. p. 72—73° (Found: C, 76·1; H, 11·3. $C_{16}H_{28}O_2$ requires C, 76·2; H, 11·1%). (ii) A mixture of amyl amyl*iso*propenyl ketone (20 g.), cyanoacetamide (8·5 g.), and alcoholic sodium ethoxide (0·5 g. of sodium in 50 c.c.) was refluxed for 1 hour. The solution was poured into dilute sulphuric acid, and the solid collected (18 g., colourless plates, m. p. 215°, from alcohol). This material was refluxed for 4 hours with sulphuric acid (50 c.c.), acetic acid (100 c.c.), and water (60 c.c.), then added to water, and the acid product collected by means of ether. It was esterified by boiling for 3 hours with alcohol (100 c.c.) and sulphuric acid (5 c.c.). The *ester* was a colourless oil, b. p. 185—188°/12 mm. (Found: C, 72·3; H, 11·4. $C_{18}H_{34}O_3$ requires C, 72·5; H, 11·4%). The semicarbazone of the corresponding acid (a viscous oil) separated from alcohol in colourless prisms, m. p. 98°. An attempt to apply the Wolff–Kishner reduction process to this semicarbazone was unsuccessful. After acid hydrolysis of the product, the unchanged keto-acid was recovered as the ester, b. p. 185—190°/13 mm., hydrolysed to the keto-acid and recognised as the semicarbazone, m. p. 98°.

Some non-ketonic material was obtained by reduction of the acid according to Clemmensen (ester, b. p. 170—175°/11 mm.), but the process was unsatisfactory and was not further investigated.

5-Methyl-2-n-nonyl-5-n-decylcyclohexane-1 : 3-dione.—Methylaniline (12 g.) in benzene (25 c.c.) was added to a Grignard solution prepared from ethyl bromide (16 g.), magnesium (3 g.), and ether (40 c.c.). This mixture was gradually added during ½ hour to a cooled and stirred solution of methyl *n*-decyl ketone (32 g.) in benzene (30 c.c.). After 10 hours, dilute hydrochloric acid was added, and the product isolated and distilled after addition of a trace of iodine. The pale yellow oil (18 g.), b. p. 235°/14 mm., is assumed from close analogies to be *n*-decyl *β-n-decylisopropenyl* ketone.

A mixture of this *αβ*-unsaturated ketone (6 g.), ethyl malonate (4 g.), and alcoholic sodium ethoxide (0·5 g. of sodium in 10 c.c.) was refluxed for 4 hours. Potassium hydroxide (10 g.) in water (15 c.c.) was then added, and refluxing continued for 2 hours. Acidification after pouring into water precipitated an oil that gradually solidified. The *substance* crystallised from a little acetone in colourless needles (4 g.), m. p. 69° (Found: C, 79·3; H, 12·2. $C_{26}H_{48}O_2$ requires C, 79·6; H, 12·2%). It gave a pale brown coloration in alcoholic ferric chloride.

Ethyl 5-Keto-3-methyl-3-n-decylpentadecoate.—A mixture of the decyl decyl*iso*propenyl ketone (41 g.), cyanoacetamide (9 g.), and alcoholic sodium ethoxide (2·5 g. of sodium in 100 c.c.) was refluxed for 6 hours. It was then poured into dilute sulphuric acid, and the gummy solid collected. It was refluxed with sulphuric acid (30 c.c.), acetic acid (100 c.c.), and water (40 c.c.) for 5 hours. The acidic product was isolated, converted into its *ethyl* ester, and distilled, b. p. 245—250°/13 mm. (Found: C, 76·5; H, 12·1. $C_{38}H_{74}O_3$ requires C, 76·7; H, 12·3%). Acid hydrolysis afforded the corresponding acid, b. p. 265—270°/10 mm.

Neither the ester nor the acid could be reduced by Clemmensen's method even under the most vigorous conditions and in presence of toluene and acetic acid. The unchanged material was recognised by re-esterification and cyclisation to the above dihydroresorcinol derivative.

Experiments with Pinacols.—2-Methyl-3-*n*-amyloctane-2 : 3-diol was obtained, by the action of *n*-amylmagnesium bromide on ethyl α-hydroxy*iso*butyrate in ethereal solution, as a colourless oil, b. p. 150—160°/10 mm., that solidified after a long time as a mass of fibrous crystals, m. p. *ca.* 35°. The main product, b. p. 60—65°/10 mm., appeared to be a hydrocarbon. This pinacol was converted by cold concentrated sulphuric acid into a ketonic substance (2 : 4-dinitrophenylhydrazone), a pale yellow oil having a pleasant odour, and oxidation of this pinacolone with boiling 33% nitric acid gave a mixture of acids. The fraction, b. p. 150—210°, furnished a crystalline amide, m. p. 117° (Found: N, 9·0. $C_9H_{19}ON$ requires N, 9·0%). Hence this is probably *2 : 2-dimethylheptamide*.

The reaction between *n*-heptylmagnesium bromide and ethyl α-hydroxy*iso*butyrate (14 g.) gave as the chief product a colourless oil (22 g.), b. p. 130°/12 mm., m. p. 3° (Found: C, 86·2; H, 13·8. $C_{18}H_{34}$ requires C, 86·4; H, 13·6%). When ethyl lactate was used, the product was of similar nature, b. p. 120—130°/14 mm., m. p. 2°. In both cases very little material of higher b. p. was produced.

n-Dodecylmagnesium bromide and ethyl α-hydroxy*iso*butyrate (13·2 g.) gave dodecane (10 g., b. p. 212—215°) and

a solid (21 g.) which crystallised from alcohol in plates, m. p. 53—54° (Found: C, 85·4; H, 14·5. $C_{28}H_{56}$ requires C, 85·7; H, 14·3%). The same substances were obtained by the action of magnesium on a mixture of dodecyl bromide and ethyl hydroxy*iso*butyrate in ethereal solution.

The action of amalgamated magnesium on methyl *n*-decyl ketone (20 g.) gave a poor yield of the pinacol (2 g., b. p. 240—250°/12 mm.), recognised as such by oxidation with lead tetra-acetate, whereby methyl decyl ketone was produced (semicarbazone, m. p. 121°). The action of cold concentrated sulphuric acid on this material gave a ketone (0·8 g., b. p. 200—240°/12 mm.). The reduction of methyl decyl ketone by sodium in moist ether afforded dodecan-2-ol and only traces of material of higher b. p.

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89. *The Magnitude of the Solvent Effect in Dipole-moment Measurements. Part VI. Induced and Mesomeric Moments of the Alkyl Halides and the Halogenobenzenes.*

By ARNOLD AUDSLEY and FRANK R. GOSS.

The influence on the primary moment (μ_P) of alkyl radicals, known as the radical effect, is due to moments (μ_I) induced in the alkyl chains which, unlike the actual inductive effects, are not proportional to μ_P. This is due to a spatial effect arising from the disposal of the polarisable matter about the dipole axis which varies independently of the ratio μ_I/μ_P but can be determined simultaneously with the dipole moment by making use of the solvent-effect equation developed earlier in this series. In Part V (this vol., p. 358) we found that the radical effect consists of three parts, and it is now shown that the influence of the spatial effect on each of these parts varies through a series of alkyl halides in the order AlkF > AlkCl > AlkBr > AlkI. The spatial effect is negligible for the alkyl iodides, whence it is shown that the true μ_I/μ_P ratio for the tertiary halides is 0·410, and that this can be applied to analogous halogen compounds; hence we have calculated the mesomeric moments (μ_M) for the aromatic series. These values of μ_M for the halogens can be expressed as a linear function of the atomic number (Z) in the formula $\mu_M = 1{\cdot}15 - 0{\cdot}012Z$, and consequently they follow the known order for the mesomeric effect F > Cl > Br > I. They are in good agreement with those obtained by Groves and Sugden (J., 1937, 1992) by quite a different method of approach. The corrected moments for the halogenobenzenes follow the sequence PhI > PhBr > PhCl > PhF, earlier values for iodobenzene being too low owing to neglect of the solvent effect, which follows the sequence PhI ≫ PhBr > PhCl > PhF.

THE total dipole moment of the simpler organic compounds can be expressed as the sum of a primary moment μ, arising in the bond C—X where X is the polar group, an induced moment μ_I, which is the vectorial component of the inductive effects in the carbon chain, and a mesomeric moment μ_M, if there is any mesomeric effect associated with the molecule. This conception was stated by Sutton (*Proc. Roy. Soc.*, **1931**, *A*, **133**, 668; cf. Ingold, *Chem. Reviews*, **1934**, **15**, 254), who expressed the total moment as an algebraic sum $\mu = \mu_P + \mu_I + \mu_M$. He made the comparison between *tert.*-butyl and phenyl compounds because the relevant components of the moments induced in the C—C bonds of the benzene ring by the primary moment could be assumed to correspond with, and for practical purposes be equal to, those of the *tert.*-butyl radical. The difference between these values was then taken as equal to the mesomeric moment. This procedure may lead to fallacious results for two reasons: (i) the moments used for both the aliphatic and the aromatic compounds have been those measured in dilute solution, and have lacked a correction for the solvent effect; (ii) no account has been taken of the effect of the shape of the radical on the induced moments. Calculations dealing with this spatial effect were made by Frank (*Proc. Roy. Soc.*, **1935**, *A*, **152**, 171).

It is not practicable, in order to overcome the first difficulty, to measure all the required moments in the vapour state, because, as Groves and Sugden (J., **1937**, 158) have shown, the vapours of some of the *tert.*-butyl halides decompose too rapidly. We now obviate this difficulty by correcting solution values by means of the solvent-effect equation as described in earlier parts of this series (see Part V, *loc. cit.*); this solvent correction is particularly large for iodobenzene, which has a solvent-effect constant [K] of 2·28, the largest yet determined. The radical effect of the induced moments has, in the case of the alkyl iodides, been shown (*ibid.*) to consist of three parts: (*a*) a large induced moment for the sequence Me, Et, Pr^{β}, Bu^{γ}; (*b*) a small series induced moment not noticeable beyond the butyl compounds; and (*c*) a series decrement which appears to continue right along the alkyl chains. These three parts of the radical effect were interpreted on the basis of Frank's calculation that the induced moments only augment the primary moment if the bulk of the polarisable matter is introduced along, or near to, the axis of the dipole.

In order to overcome the second difficulty, the investigation of the spatial effect on these three parts of the radical effect has now been extended to alkyl fluorides, chlorides, and bromides. For the purpose of following changes in the spatial effect it is fortunate that, by measuring the polarisation of suitable liquid mixtures and applying the solvent-effect equation, we can obtain (see Table I), not only the corrected dipole moments, but also the solvent-effect constants [K] which, as explained in Part V, give a measure of the proportion of the polarisable matter of the molecule which is disposed in the line of the dipole. These constants decrease in the order in which the halogen atoms affect the length of the polar axis, I > Br > Cl > F, and if plotted against the atomic numbers of the appropriate halogens, they lie on smooth equidistant curves, which are moreover of considerable value in checking the accuracy of the experimental data. The value of [K] for *tert.*-butyl chloride is of special interest, for although the molecule has a large moment [$\mu = 2{\cdot}04$ D.; Wiswall and Smyth

TABLE I.

Polarisation constants of carbon tetrachloride solutions at 20°.

	Calculated values.*			Exptl. value.	Derived poln. coeffs.			Solvent-effect constant,	Corr. dipole moment,
	P_{E+A}.	P_E.	P_A.	P_∞.	Z.	Y.	P_0.	$[K]$.	μ, D.
Methyl fluoride	12·1	6·5	5·6	} vapour values [1]					{ 1·76
Ethyl fluoride	16·6	11·0	5·6						{ 1·84
n-Amyl fluoride	30·2	24·6	5·6	70·2	117·5	87·6	35·6	0·87	1·30
tert.-Butyl fluoride	calculated (see text)								[1·72]
tert.-*Amyl fluoride*	30·7	25·1	5·6	88·6	132·0	127·4	49·9	0·75	1·54
Methyl chloride	15·4	11·3	4·1	} vapour values [2]					{ 1·84
Ethyl chloride	19·9	15·8	4·1						{ 2·01
n-Butyl chloride	29·0	24·9	4·1	106·3	88·4	171·6	76·1	1·13	1·90
tert.-Butyl chloride	see Part IV (J., 1941, 864)							0·99	2·04
Methyl bromide	19·1	14·1	5·0	vapour value [1]					1·72
Ethyl bromide	see Part IV								1·99
n-Butyl bromide	32·7	27·7	5·0	107·2	78·8	165·5	79·7	1·36	1·95
tert.-Butyl bromide	33·3	28·3	5·0	131·1	92·9	217·4	99·4	1·22	2·17
Methyl iodide	} see Part IV (*loc. cit.*)							1·72	1·56
Ethyl iodide								1·62	1·89
n-Butyl iodide	} see Part V (*loc. cit.*)							1·49	1·93
tert.-Butyl iodide								1·36	2·20
Fluorobenzene	} see Part IV (*loc. cit.*)							1·44	1·44
Chlorobenzene								1·61	1·64
Bromobenzene								1·88	1·68
Iodobenzene	41·4	38·3	3·1	77·8	23·2	81·1	60·0	2·28	1·69

* Calculated from the contributory values for P_E and $P^{liq.}_{E+A}$ recorded in J., 1941, 864, Table II. Using these additive P_{E+A} values, moments have been recalculated from the vapour data of:

[1] Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499. [2] Fuchs, *Z. Physik*, 1930, **63**, 824.

(*J. Chem. Physics*, 1941, **9**, 356) record 2·13, but this value is not corrected for P_{E+A}], it is practically spherical as shown by the similarity in the polarisability of the Cl and Me groups (P_E values are F 0·9, Cl 5·7, Br 8·5, I 13·2, Me 5·6 c.c.). This nearly symmetrical character for the *tert.*-butyl chloride molecule, which has been deduced by Baker and Smyth (*J. Amer. Chem. Soc.*, 1939, **61**, 2798) from its freedom of rotation in the solid state, is now confirmed by our determination of $[K]$, which is 0·99, or very nearly unity, and this, by definition, is the value for symmetrical compounds.

The moments of the alkyl halides are given in Table I. Values for the volatile compounds are obtained from recorded vapour data, and made comparable with our corrected liquid values by employing throughout additive P_{E+A} coefficients, calculated from the atomic contributions tabulated in Part IV (*loc. cit.*). Our values for *n*-butyl chloride and bromide are lower than those recorded (Smyth and McAlpine, *J. Chem. Physics*, 1935, **3**, 347; Groves and Sugden, *loc. cit.*) for the vapours by the same amount as that attributed (see Part V) in the case of *n*-butyl iodide to a different disposition of the alkyl chain in the liquid and the vapour state. The value for *tert.*-butyl fluoride has had to be calculated indirectly, as this compound is both too volatile for accurate determination in the liquid state, and too unstable for vapour measurements (cf. Cooper and Hughes, J., 1937, 1183). We have found (see Part V) that tertiary and primary iodides have the same series decrement, so that for the tertiary fluorides has been determined from the difference between the *n*-amyl and the ethyl member $(1{\cdot}84—1{\cdot}30)/3 = 0{\cdot}18$. This decrement has been applied to the value for *tert.*-amyl fluoride (1·54), giving the calculated moment for *tert.*-butyl fluoride as 1·72 D.

From our definition of the solvent-effect constant (see Part V) and Frank's calculation of the influence of the spatial effect on the radical effect, the apparent direction of the induced moments (*a*) in the sequence Me, Et, Pr^β, Bu^γ should be opposed to their true direction, when the value of $[K]$ falls below unity. This prediction is precisely borne out by our results, particularly those for *tert.*-butyl fluoride. The radical effect (*a*) is undoubtedly reversed for the fluorides; further, the data show that all three parts of the radical effect exhibit a decrease with the falling values of $[K]$ in the series $I > Br > Cl > F$, the small series inductive effect (*b*) observed for the lower iodides tending to disappear at the lower values of $[K]$, whilst the series decrement (*c*) along the alkyl chains becomes more prominent, being 0·01, 0·04, and 0·07 for the iodides, bromides, and chlorides, until for the fluorides it reaches the large value of 0·18 D. already noted.

These relationships between $[K]$ and μ enable us to conclude that the true induced moments in the alkyl halides are successively masked in passing down the series I, Br, Cl, F by changes in the disposal of the polarisable matter about the C—X bond arising from the decreasing radius of the halogen atoms. If we could imagine an alkyl series where such spatial considerations did not affect the induced moments, the observed moments for a lengthening chain might be expected (cf. Smyth and Rogers, *J. Amer. Chem. Soc.*, 1930, **52**, 2237) to reach a constant value. This is very nearly the case for the iodides, which with their small series decrement of 0·01 D. must suffer little or no spatial effect. We are therefore justified in concluding that for the iodides the spatial effect can be neglected in comparison with the other manifestations of the radical effect, which means that the radical effect for the Me, Et, Pr^β, Bu^γ sequence can, in the case of the iodides, be taken to represent the true induced moments of these groups.

Following Groves and Sugden (*loc. cit.*), we assume that the primary moment is identified with the moment of the methyl halide, and any error so introduced has only a negligible effect on our subsequent calculations. The order of μ_P for the C—X bonds, Cl > F > Br > I, is not precisely the same as that of the inductive ($-I$) effect, F > Cl > Br > I, but as Ingold (*loc. cit.*, p. 240) says, this order must be partly upset for dipole moments by the apparent size of the halogen atoms, which are in the reverse order F < Cl < Br < I. Now, we have shown in the previous paragraph that the moment of *tert.*-butyl iodide should give us the true inductive ratio μ_I/μ_P for the tertiary halides, free from spatial effect. This ratio is 0·64/1·56, or 0·410, which should therefore give, not only the true induced moment in all the tertiary halides as recorded in Table II, but also the observed induced moments in analogous halogen compounds, for which the spatial effect is negligible and $[K]$ is therefore large. It is accordingly the appropriate ratio for the halogenobenzenes, as these all have $[K]$ greater than any of the *tert.*-alkyl halides, and it is also in good agreement with the value of 0·433 calculated by Groves and Sugden (*loc. cit.*). The mesomeric moments recorded in this paper (Table II) and calculated from the relation $\mu = \mu_P + \mu_I + \mu_M$ are therefore of the same order of magnitude as those obtained by Groves and Sugden, although there are small deviations due to the employment by them of only partly corrected solution data for fluoro- and iodo-benzene. These values of μ_M for the halogens can be expressed as a linear function of the atomic number (Z) in accordance with the equation $\mu = 1{\cdot}15 - 0{\cdot}012Z$, and are therefore in the order F > Cl > Br > I established by Baddeley and Bennett (J., 1933, 261; cf. Bird and Ingold, J., 1938, 918) for the mesomeric effect.

New polarisation data are presented in Table I for the polar liquids in mixtures with carbon tetrachloride dealt with in this paper. From these data the dipole moments and solvent-effect constants have been calculated by the usual solvent-effect method. Moments recalculated from previously recorded vapour data, by making use of the additive P_{E+A} values tabulated in Part IV, are also included.

TABLE II.

Primary, induced, and mesomeric moments of tert.*-halides and halogenobenzenes.**

	MeX (μ_P).	μ_I (0·64 μ_P/1·56).	$\mu_P + \mu_I$.	PhX ($\mu_P + \mu_I + \mu_M$).	μ_M.
F	1·76	−0·72	−2·48	−1·44	+1·04
Cl	1·84	−0·75	−2·59	−1·64	+0·95
Br	1·72	−0·70	−2·42	−1·68	+0·74
I	1·56	−0·64	−2·20	−1·69	+0·51

* Values in the last four columns have been assigned their appropriate algebraic signs.

The newly recorded value for the moment of iodobenzene is considerably higher than those already published owing to the unusually large solvent-effect correction associated with the large $[K]$ for this substance (see above). Further, the moments of the halogenobenzenes fall into a regular sequence PhI > PhBr > PhCl > PhF; this order arises from the fact that, although the mesomeric moments decrease in the direction F > Cl > Br > I, the fall in their magnitude is much more rapid than the corresponding fall in the magnitude of the induced moments which are of opposing sign (see Table II). The moments of the *tert.*-butyl halides are also in the reversed order $Bu^tI > Bu^tBr > Bu^tCl > Bu^tF$, but this is due entirely to the operation of the spatial effect dealt with in this paper. Anomalous radical effects noted by Cowley and Partington (J., 1938, 977) and by Groves and Sugden (J., 1937, 158) arise from the same cause.

EXPERIMENTAL.

Density, dielectric constant, and temperature were measured as previously described (Goss, J., 1933, 1343; 1935, 730; 1940, 593).

Preparation and Purification of Materials.—*tert.-Amyl fluoride* is new. It was obtained by distillation of the middle fraction of a Kahlbaum sample of *tert.*-amyl alcohol with excess of 40% hydrofluoric acid. Unsaturated impurities were removed with bromine at 0°, and the fluoride washed with sodium bicarbonate solution and water. After being dried with sodium sulphate it was distilled twice, the lower fraction, b. p. 38°/458 mm., being collected. This fluoride decomposes on distillation at atmospheric pressure and on keeping; as it was not analysed before this occurred and as no further material was available, no better analyses could be obtained (Found: C, 68·2; H, 13·4. $C_5H_{11}F$ requires C, 66·6; H, 12·3%). However, the physical constants now recorded are those of the pure fluoride, measured before decomposition had commenced.

TABLE III.

Criteria of purity.

	Observed.		Previously recorded.			Observed.		Previously recorded.	
	$d_4^{20°}$.	$n_D^{20°}$.	$d_4^{20°}$.	$n_D^{20°}$.		$d_4^{20°}$.	$n_D^{20°}$.	$d_4^{20°}$.	$n_D^{20°}$.
n-Amyl fluoride	0·7885	1·3634	0·7880 [1]	1·3580 [1]	*n*-Butyl bromide ...	1·2758	1·4399	1·2756 [3]	1·4397 [3]
tert.-Amyl fluoride ...	0·7780	1·3680	—	—	*tert.*-Butyl bromide	1·2220	1·4283	1·2209 [4]	1·4281 [4]
n-Butyl chloride ...	0·8846	1·4017	0·8865 [2]	1·4024 [2]	Iodobenzene	1·8307	1·6206	1·8306 [5]	1·6202 [5]

[1] Swarts, *Bull. Soc. chim. Belg.*, 1921, **30**, 302. [2] Timmermans and Hennaut-Roland, *J. Chim. physique*, 1930, **27**, 401. [3] Timmermans and Martin, *ibid.*, 1926, **23**, 745. [4] Timmermans and Delcourt, *ibid.*, 1934, **31**, 85. [5] Timmermans and Hennaut-Roland, *ibid.*, 1932, **29**, 529.

n-Amyl fluoride was prepared from the iodide (this vol., p. 366) by the method of Swarts (*loc. cit.*), fluorination being carried out with mercurous fluoride (Henne and Renoll, *J. Amer. Chem. Soc.*, 1938, **60**, 1060). It was twice fractionally distilled, the middle fraction being collected in each case.

tert.-Butyl bromide, prepared by a method similar to that for the chloride (*Organic Syntheses*, 1928, **8**, 50) from

recrystallised *tert.*-butyl alcohol (B.D.H.), was washed with ice-cold 1% sodium bicarbonate solution and fractionated (250 mm.), the middle third being collected.

n-Butyl chloride and bromide were prepared from *n*-butyl alcohol (*ibid.*, 1925, **5**, 27; 1921, **1**, 2) and fractionated, the middle third being collected in each case.

TABLE IV.

Polarisations of carbon tetrachloride mixtures at 20°.

c_2.	ϵ.	$d_4^{20°}$.	P_{12}.	$P_{\infty 2}$.	$P_{\infty 1}$.	c_2.	ϵ.	$d_4^{20°}$.	P_{12}.	$P_{\infty 2}$.	$P_{\infty 1}$.
					n-*Amyl fluoride.*						
0·00000	2·2394	1·5940	28·21	70	28·2	0·02397	2·2915	1·5713	29·17	69	28·3
0·00472	2·2503	1·5893	28·41	70	28·2	0·04964	2·3491	1·5480	30·19	69	28·3
0·00649	2·2540	1·5878	28·48	70	28·2	1·00000	4·242	0·7885	59·37	59·4	35
0·01292	2·2686	1·5818	28·74	70	28·2						
					tert.-*Amyl fluoride.*						
0·00000	2·2384	1·5942	28·20	89	28·2	0·05508	2·4164	1·5401	31·30	82	28·3
0·00718	2·2629	1·5864	28·64	88	28·2	0·13046	2·6753	1·4723	35·42	80	29
0·01358	2·2845	1·5800	29·02	88	28·2	0·34531	3·420	1·2847	45·82	74	31
0·02652	2·3284	1·5667	29·80	87	28·3	1·00000	5·888	0·7780	71·80	71·8	42
					n-*Butyl chloride.*						
0·00000	2·2386	1·5940	28·20	106	28·2	0·17450	3·062	1·4622	39·88	88	30
0·00888	2·2798	1·5871	28·88	105	28·2	0·23031	3·362	1·4211	43·31	85	31
0·01760	2·3213	1·5804	29·55	103	28·2	0·36797	4·056	1·3206	50·17	78	34
0·04055	2·4275	1·5630	31·22	101	28·3	0·43800	4·424	1·2707	53·27	76	36
0·06086	2·5232	1·5475	32·66	98	28·4	0·48141	4·646	1·2400	55·01	75	37
0·10809	2·7495	1·5121	35·86	94	28·9	0·74153	6·028	1·0588	64·12	72	42
0·14211	2·9043	1·4864	37·91	91	29·2	1·00000	7·398	0·8846	71·23	71·2	47
					n-*Butyl bromide.*						
0·00000	2·2384	1·5942	28·20	107	28·2	0·09722	2·7001	1·5608	35·27,	95	28·8
0·00812	2·2774	1·5914	28·84	106	28·2	0·20833	3·256	1·5232	42·36	86	31
0·01368	2·3025	1·5894	29·26	105	28·2	0·45559	4·478	1·4425	54·41	76	36
0·02483	2·3537	1·5855	30·09	103	28·3	0·76412	5·985	1·3463	65·37	72	42
0·05046	2·4764	1·5767	32·00	100	28·4	1·00000	7·099	1·2758	71·98	72·0	46
					tert.-*Butyl bromide.*						
0·00000	2·2384	1·5942	28·20	131	28·2	0·06688	2·6624	1·5643	34·81	121	28·6
0·00437	2·2650	1·5922	28·64	130	28·2	0·13988	3·170	1·5365	41·37	112	30
0·00693	2·2802	1·5911	28·89	130	28·2	0·19850	3·574	1·5075	46·10	106	32
0·00758	2·2850	1·5909	28·97	130	28·2	0·42977	5·385	1·4236	61·15	92	38
0·00898	2·2932	1·5901	29·11	129	28·2	0·60152	6·815	1·3601	69·71	87	43
0·01506	2·3312	1·5873	29·74	128	28·2	0·71839	7·789	1·3179	74·59	85	46
0·03395	2·4491	1·5790	31·61	126	28·3	1·00000	10·248	1·2220	84·66	84·7	53
					Iodobenzene.						
0·00000	2·2355	1·5938	28·16	79	28·2	0·14558	2·6332	1·6331	34·78	73	28·5
0·00539	2·2524	1·5953	28·45	79	28·2	0·23074	2·8860	1·6549	38·58	70	28·8
0·01230	2·2711	1·5972	28·78	79	28·2	0·42784	3·414	1·7030	45·90	66	31
0·02447	2·3087	1·6006	29·42	78	28·2	0·63496	3·895	1·7549	51·96	63	33
0·04598	2·3701	1·6064	30·47	77	28·3	1·00000	4·625	1·8306	60·98	61·0	37
0·08908	2·4936	1·6180	32·52	75	28·4						

Iodobenzene, prepared from " AnalaR " aniline (Gattermann, " Laboratory Methods of Organic Chemistry," 1932, p. 278), was washed with sodium thiosulphate solution, dilute sulphuric acid, sodium hydroxide solution, and water, dried with calcium chloride, and twice fractionally distilled at 16 mm.

The criteria of purity for these compounds are recorded in Table III.

Results.—The experimental data and the partial polarisations ($P_{\infty 2}$ for the polar components, $P_{\infty 1}$ for the carbon tetrachloride), obtained as intercepts of the tangents to the P_{12}–c_2 curve at the axes where $c_2 = 0$ and $c_2 = 1$, are all recorded in Table IV.

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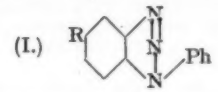
90. *The Graebe–Ullmann Synthesis of Carbazole Derivatives. Preparation and Synthesis of* 1*-Nitrocarbazole.*

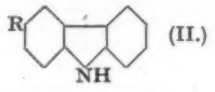
By ROBERT W. G. PRESTON, S. HORWOOD TUCKER, and (in part) JAMES M. L. CAMERON.

Carbazole derivatives containing unsaturated substituents, *e.g.*, nitro, acetyl, cyano, have, contrary to former experience, been obtained by pyrogenesis from the corresponding triazoles. In particular, 1-nitrocarbazole has been thus synthesised. Its preparation by nitration of carbazole, and separation from the 3-isomer by chromatographic analysis, are described. 1-Nitrocarbazole has also been synthesised from 3 : 6-bistrichloroacetylcarbazole—a process in which it is prepared free from 3-nitrocarbazole.

IN the Graebe–Ullmann synthesis of carbazole (*Annalen*, 1896, **291**, 16) the last step is completed by heating 1-phenyl-1 : 2 : 3-benztriazole (I; R = H). The preparation of carbazole derivatives by this method proceeds

smoothly when the substituent is a saturated group, *e.g.*, amino or alkyl, but when an unsaturated group such as nitro, acetyl, or cyano is present in either benzene ring of the triazole, conversion into the corresponding

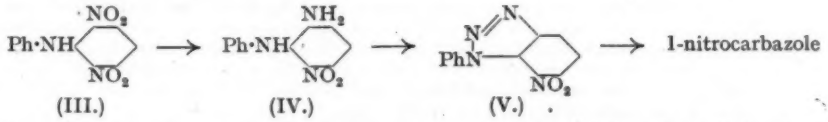




carbazole has not hitherto been accomplished (see *Arch. Sci. phys. nat.*, 1904, **17**, 88; *Annalen*, 1911, **379**, 168; *Ber.*, 1916, **49**, 2231, 2237; *Helv. Chim. Acta*, 1921, **4**, 1036; J., 1932, 2188; 1935, 741. On the other hand cf. *Annalen*, 1904, **332**, 82; *Arch. Sci. phys. nat.*, 1904, **17**, 78; *J. Amer. Chem. Soc.*, 1931, **53**, 4183; J., 1932, 2188).

We have been successful in bringing about the triazole ⟶ carbazole (I ⟶ II) reactions, where R = NO_2, COMe, CN, giving yields of a trace, 22% and 34% respectively. The synthesis of 3-acetylcarbazole by this unambiguous method confirms the work of Plant and Williams (J., 1934, 1142), who prepared 3-acetylcarbazole and settled its constitution by other methods.

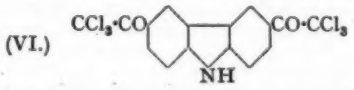
The conversion of 7-nitro-1-phenyl-1 : 2 : 3-benztriazole into 1-nitrocarbazole (18%) by the Graebe–Ullmann method was effected as outlined below :



2 : 6-Dinitrodiphenylamine (III) was prepared by the action of 1-chloro-2 : 6-dinitrobenzene on aniline, and also by decarboxylation of 2 : 6-dinitrodiphenylamine-4-carboxylic acid. A deep red by-product, which is possibly 1-*nitrophenazine*, was isolated in the latter case.

The nitration of carbazole gives a mixture of 1-nitrocarbazole (4%) and 3-nitrocarbazole (75%) (Lindemann and Werther, *Ber.*, 1924, **57**, 555, 1316; Lindemann and Wessel, *ibid.*, 1925, **58**, 1221), the separation of which by Morgan and Mitchell's method (J., 1931, 3283) gave capricious results in our hands, but was easily accomplished by chromatographic analysis with benzene as solvent and elution reagent : 1-nitrocarbazole (6%) was eluted first and 3-nitrocarbazole (70%) followed very slowly. Three methods of nitration were adopted : (*a*) Ziersch's method (*Ber.*, 1909, **42**, 3797), (*b*) fuming nitric acid in acetic anhydride, (*c*) potassium nitrate in glacial acetic acid–acetic anhydride.

The following synthetic method provides 1-nitrocarbazole free from 3-nitrocarbazole : Carbazole was converted by the action of trichloroacetonitrile, anhydrous aluminium chloride, and hydrogen chloride in chlorobenzene, followed by acid hydrolysis, into 3 : 6-bistrichloroacetylcarbazole (VI) (Dunlop and Tucker, J., 1939, 1954; and this paper). Nitration by concentrated nitric acid in glacial acetic acid gave the 1-*nitro*-derivative (VII), which by alkaline hydrolysis afforded 1-*nitrocarbazole*-3 : 6-*dicarboxylic acid*. Decarboxylation in quinoline–copper gave 1-nitrocarbazole.



1-Nitrocarbazole was also prepared by the conversion of 3 : 6-bistrichloroacetylcarbazole (VI) into ethyl carbazole-3 : 6-dicarboxylate by treatment with sodium in ethyl alcohol (Houben and Fischer, *Ber.*, 1931, **64**, 240, 2636), this method, contrary to Houben and Fischer's general finding, being preferable to the use of potassium acetate in alcohol. The ester on nitration gave *ethyl* 1-*nitrocarbazole*-3 : 6-*dicarboxylate*, which on hydrolysis and decarboxylation gave 1-nitrocarbazole.

3-*Cyano*- and 3 : 6-*dicyano-carbazole* have been prepared from carbazole by the Houben–Fischer method (*Ber.*, 1930, **63**, 2464; 1933, **66**, 339. See Dunlop and Tucker, *loc. cit.*, p. 1949).

Experimental.

Graebe–Ullmann Syntheses.

3-*Nitrocarbazole*.—2 : 4-Dinitrodiphenylamine, m. p. 153°, was prepared by heating 1-chloro-2 : 4-dinitrobenzene (20 g.; 1 mol.) with aniline (10 g.; 1·1 mols.) until the vigorous reaction which set in had subsided, then raising the temperature to the b. p. The product, after crystallisation from glacial acetic acid (yield, 100%) (cf. Reissert and Goll, *Ber.*, 1905, **38**, 93), was reduced to 4-nitro-2-aminodiphenylamine (Ullmann, *Annalen*, 1904, **332**, 98). Diazotisation to give 5-nitro-1-phenyl-1 : 2 : 3-benztriazole was accomplished by means of excess of sodium nitrite in excess of hot glacial acetic acid—the method adopted for all triazoles subsequently described (cf. Nietzki, *Ber.*, 1895, **28**, 2971). The triazole, in portions, was carefully heated over a free flame. The product, dissolved in glycol methyl ether, gave unchanged triazole and, on standing and scratching, a trace of 3-nitrocarbazole, m. p. 213°.

3-*Acetylcarbazole*.—4-Bromo-3-nitroacetophenone (Borsche *et al.*, *Ber.*, 1916, **49**, 2235) was prepared by dissolving *p*-bromoacetophenone (20 g.) in fuming nitric acid (*d* 1·52; 150 ml.) at 0° (yield, 19 g.; 78%). When nitric acid, *d* 1·50, was used, *p*-bromoacetophenone was recovered unchanged, unless the temperature was allowed to rise during nitration; a substance, m. p. 175—176°, was then obtained which was probably 4-*bromo*-3 : 5-*dinitroacetophenone* (Found : N, 9·8. $C_8H_5O_5N_2Br$ requires N, 9·7%).

4-Bromo-3-nitroacetophenone (6 g.), aniline (20 g.), and anhydrous potassium carbonate (2 g.) were heated together

(15 minutes), the product treated with dilute hydrochloric acid, and the residue crystallised from alcohol, giving 2-nitro-4-acetyldiphenylamine (5 g.; yield, 89%).

2-Amino-4-acetyldiphenylamine was prepared by reduction of the above nitro-compound by stannous chloride, glacial acetic acid, and hydrochloric acid (yield, 68%). Diazotisation gave 5-acetyl-1-phenyl-1 : 2 : 3-benztriazole (yield, 62%). The triazole (1 g.) was heated over a free flame until a slight explosion ensued. The solid, extracted with alcohol (charcoal), crystallised from toluene in straw-coloured laminæ, m. p. 165—167°, of 3-acetylcarbazole (0·2 g.; yield, 22%) (Found: N, 6·5. Calc.: N, 6·7%).

3-Cyanocarbazole.—2-Nitro-4-cyanodiphenylamine (Schöpff, *Ber.*, 1890, **23**, 3442; Borsche *et al.*, *loc. cit.*) was prepared by heating equimolecular quantities of aniline and 4-chloro-3-nitrobenzonitrile (Dunlop, Macrae, and Tucker, J., 1934, 1676) to the b. p. (yield, 78%). Reduction (stannous chloride, glacial acetic acid, hydrochloric acid) gave 2-amino-4-cyanodiphenylamine (yield, 78%), diazotisation of which gave 5-cyano-1-phenyl-1 : 2 : 3-benztriazole (yield, 65%). The triazole (1 g.) was heated (metal bath) until evolution of nitrogen ceased. Extraction with ethanol (charcoal) and crystallisation from toluene gave *3-cyanocarbazole* in colourless needles, m. p. 184—185° (0·3 g.; yield, 35%) (Found: C, 81·2; H, 4·0; N, 14·5. $C_{13}H_8N_2$ requires C, 81·25; H, 4·2; N, 14·6%).

3-Cyanocarbazole was also prepared by the Houben–Fischer method (*Ber.*, 1930, **63**, 1933): carbazole was treated with trichloroacetonitrile as for the preparation of carbazole-3-carboxylic acid (Dunlop and Tucker, *loc. cit.*, p. 1953; this paper, later), but the reaction mixture was not treated with acid; instead, more chlorobenzene was added, and dry ammonia passed to precipitate aluminium. The liquid was filtered, and the residue extracted with hot chlorobenzene and finally with ether. The united filtrates were shaken with potassium hydroxide (dry powder). The brown precipitate, mixed with the excess of potassium hydroxide, when treated with water and then with dilute hydrochloric acid, gave 3-cyanocarbazole. A small amount was obtained from the chlorobenzene–ether solution.

Similarly, by using the quantities given for the preparation of carbazole-3 : 6-dicarboxylic acid by the improved method described on p. 503, *3 : 6-dicyanocarbazole* was obtained in colourless microcrystals from nitrobenzene (followed by sublimation), unmelted at 360° (Found: C, 77·4; H, 3·3; N, 19·3. $C_{14}H_7N_3$ requires C, 77·4; H, 3·2; N, 19·35%).

3-Cyano-9-acetylcarbazole, obtained by heating 3-cyanocarbazole with acetic anhydride in presence of a trace of concentrated sulphuric acid, crystallised from glacial acetic acid in silky needles, m. p. 197—199° (Found: C, 76·7; H, 3·9; N, 11·7. $C_{15}H_{10}ON_2$ requires C, 76·9; H, 4·3; N, 12·0%).

1-Nitrocarbazole (*Graebe–Ullmann Synthesis*).—1-Chloro-2 : 6-dinitrobenzene (13·8 g.) and excess of aniline (13 g.) were heated on the boiling water-bath with shaking until (about 1 min.) the mixture became solid; the temperature was then raised just to the b. p. The product was extracted by grinding with hot dilute hydrochloric acid, and the residue crystallised from glacial acetic acid, giving 2 : 6-dinitrodiphenylamine, m. p. 107—108° (16 g.; yield, 94%) (cf. Borsche and Rantscheff, *Annalen*, 1911, **379**, 167).

A mixture of 2 : 6-dinitrodiphenylamine (5 g.), ethanol (25 ml.), and concentrated aqueous ammonia (7·5 ml.) was warmed, and hydrogen sulphide passed in until the scarlet crystals dissolved (30 mins.). The solution was boiled, filtered from sulphur, and excess of dilute hydrochloric acid added. The black precipitate, after crystallisation from alcohol, gave black-red crystals of 6-nitro-2-aminodiphenylamine, m. p. 101°, in excellent yield (cf. Borsche and Rantscheff, *loc. cit.*, p. 168).

Diazotisation with excess of sodium nitrite in glacial acetic acid (cf. Borsche and Rantscheff, *loc. cit.*) gave, from acetic acid, 7-nitro-1-phenylbenztriazole, m. p. 152°. This triazole can be sublimed; but gentle boiling of it (2·5 g.) with copper bronze (0·5 g.) over a free flame until nitrogen evolution ceased, followed by extraction with benzene, gave bronze-yellow needles of 1-nitrocarbazole (0·39 g.; yield, 18%).

Attempts were made to prepare 7-nitro-1-phenyl-1 : 2 : 3-benztriazole by the route: 2 : 6-dinitrodiphenylamine-4-carboxylic acid ⟶ 6-nitro-2-aminodiphenylamine-4-carboxylic acid ⟶ 7-nitro-1-phenyl-1 : 2 : 3-benztriazole-5-carboxylic acid; but the last could not be converted into 1-nitrocarbazole.

2 : 6-Dinitrodiphenylamine-4-carboxylic acid (Jackson and Ittner, *Amer. Chem. J.*, 1897, **19**, 18) was prepared from 4-chloro-3 : 5-dinitrobenzoic acid and aniline in boiling ethanol (yield, 96%).

2 : 6-Dinitrodiphenylamine and 1-Nitrophenazine.—The above carboxylic acid (1 g.) was boiled (15 mins.) with quinoline–copper, the solution poured into dilute hydrochloric acid, and the precipitate extracted successively with dilute aqueous ammonia and benzene (charcoal; 1 hour). The residue obtained on evaporation separated from glacial acetic acid, on dilution with a drop of water, in dark red crystals of what may be *1-nitrophenazine*, m. p. 192—195° (Found: C, 63·7; H, 3·2; N, 18·5. $C_{12}H_7O_2N_3$ requires C, 64·0; H, 3·1; N, 18·7%). The acetic acid filtrate, on scratching, deposited scarlet crystals of 2 : 6-dinitrodiphenylamine (0·1 g.; yield, 11%).

6-Nitro-2-aminodiphenylamine-4-carboxylic Acid (cf. Lindemann and Wessel, *Ber.*, 1925, **58**, 1229, 1230).—Sodium sulphide ($Na_2S,9H_2O$) (7·5 g.), sulphur (2 g.), and ethanol (1 ml.) were warmed to give a clear brown solution, which was added to a solution of 2 : 6-dinitrodiphenylamine-4-carboxylic acid (9·5 g.) in ethanol (300 ml.) and water (200 ml.) containing sodium hydroxide (1·26 g.). After 3 hours' boiling, the solution was filtered, concentrated to 400 ml., again filtered, and treated with hydrochloric acid until turbid. On cooling there separated scarlet 6-nitro-2-aminodiphenylamine-4-carboxylic acid, which, after crystallisation from ethanol, had m. p. 239° (5·7 g.; yield, 67%) (Found: C, 56·9; H, 4·2; N, 15·5. Calc. for $C_{13}H_{11}O_4N_3$: C, 57·1; H, 4·0; N, 15·4%). In absence of sodium hydroxide and water, used above, the yield was reduced to 37%.

Diazotisation and crystallisation from ethyl acetate gave colourless 7-nitro-1-phenyl-1 : 2 : 3-benztriazole-5-carboxylic acid (yield, 67%) (Found: N, 19·5. Calc. for $C_{13}H_9O_4N_4$: N, 19·7%).

Nitration of Carbazole.—(a) (Ziersch, *Ber.*, 1909, **42**, 3797; cf. Morgan and Mitchell, *loc. cit.*, p. 3284, footnote). Nitric acid (*d* 1·42; 2·3 ml., theo. 1·9 ml.) in glacial acetic acid (5 ml.) was added dropwise in 15 mins. to a shaken mixture of carbazole (5 g.) and glacial acetic acid (40 ml.) maintained at 80°. The solution was poured into water, and the yellow precipitate crystallised several times from xylene, giving 3-nitrocarbazole. The evaporated filtrates gave more of this and finally a residue, which was dissolved in benzene and chromatographed (alumina, 30 × 1·5 cm.). The first portion of the benzene eluate on evaporation gave pure 1-nitrocarbazole, and later a mixture of 1- and 3-nitrocarbazole. The mixture, crystallised from glycol methyl ether–ethanol (1 : 1), gave 1-nitrocarbazole (total, 0·43 g.; yield, 6%) and, on scratching, 3-nitrocarbazole. An upper yellow band in the chromatogram was extracted with acetone and gave more 3-nitrocarbazole (total yield, approx. 70%). A small amount of 3 : 6-dinitrocarbazole was also obtained.

(b) 1-Nitrocarbazole (6%) was obtained by the action of fuming nitric acid in acetic anhydride on carbazole at 10—15°.

Nitration of 9-acetylcarbazole gave no useful results.

1-Nitro-9-acetylcarbazole.—1-Nitrocarbazole (0·2 g.) and potassium hydroxide powder (0·4 g.) in acetone (5 ml.) were heated on the boiling water-bath, and acetic anhydride added drop by drop until the purple particles changed to yellow. After 1 hour water was added, and the precipitate crystallised from methanol (wood charcoal, ½ hour), forming long, golden-yellow, square-ended prisms of *1-nitro-9-acetylcarbazole*, m. p. 172—174° (yield, 100%) (Found: C, 66·3; H, 3·8; N, 11·3. $C_{14}H_{10}O_3N_2$ requires C, 66·1; H, 3·9; N, 11·0%).

1-Nitrocarbazole could not be acetylated by boiling with acetic anhydride containing a trace of sulphuric acid.

Synthesis of 1-Nitrocarbazole.—3 : 6-Bistrichloroacetylcarbazole (VI) (Dunlop and Tucker, *loc. cit.*) was prepared by the following slightly modified method and isolated: A mixture of carbazole (8·4 g.; 1 mol.), chlorobenzene (80 ml.), trichloroacetonitrile (12 ml.; 2·4 mols.), and anhydrous aluminium chloride (16 g.; 2·4 mols.) was treated with dry hydrogen chloride for 45 minutes. Throughout this and subsequent operations the mixture was violently shaken at frequent intervals. The colour of the solid changed from tomato-red to brown and finally the mixture became mobile. It was heated at 60° for ½ hour and at the b. p. for ½ hour, a black-green solid being obtained. Concentrated hydrochloric acid was added and, after the vigorous reaction had subsided, the chlorobenzene was removed in steam. To ensure hydrolysis, the green residue was ground, thoroughly boiled with concentrated hydrochloric acid, and again treated with steam; after washing with water the light green product (yield, 100%) was sufficiently pure for further use. [It gave no insoluble residue (carbazole) after being boiled with dilute potassium hydroxide solution.] It separated from glacial acetic acid (deep red solution) (charcoal; 1 hr.) in pale green crystals, but from a solution in acetic acid, subsequently diluted with water, in silver-grey, stellate clusters of needles, giving 3 : 6-bistrichloroacetylcarbazole, m. p. 193—195° (bottle-green melt) (Found: C, 41·8; H, 1·7; Cl, 46·3. Calc. for $C_{16}H_7O_2NCl_6$: C, 41·9; H, 1·5; Cl, 46·5%) (yield, 18·5 g.; 81%). Evaporation of the acetic acid filtrate, followed by dilution with water, sometimes yielded a small amount of 3-trichloroacetylcarbazole.

Purification of 3 : 6-bistrichloroacetylcarbazole was facilitated by boiling with acetic acid and sodium dichromate, but addition of concentrated sulphuric acid to this boiling mixture effected oxidation: a product was isolated and is being investigated.

3 : 6-Bistrichloroacetylcarbazole appeared to combine with acetic anhydride, but it could not be acetylated by boiling with the anhydride in presence of a trace of concentrated sulphuric acid. When boiled with dilute potassium hydroxide solution, it evolved chloroform and dissolved completely. The acidified solution gave carbazole-3 : 6-dicarboxylic acid (yield, 75%).

3-Trichloroacetylcarbazole was prepared (yield, 85%) by a similar procedure, the quantities formerly given (Dunlop and Tucker, *loc. cit.*, p. 1953) being used.

1-*Nitro*-3 : 6-*bistrichloroacetylcarbazole* (VII). 3 : 6-Bistrichloroacetylcarbazole (7 g.), dissolved in hot glacial acetic acid (70 ml.), was treated with concentrated nitric acid (21 ml.), and the mixture heated to the b. p. When the vigorous reaction had subsided, the mixture was boiled for 1 min.; a yellow crystalline precipitate separated from the boiling solution, which was then allowed to cool. Practically pure product (6·5 g.; yield, 83%) separated. 1-*Nitro*-3 : 6-*bistrichloroacetylcarbazole* separated from acetic anhydride in pale yellow crystals, which slowly lost acetic anhydride of crystallisation on standing or on treatment with acetic acid and became bright yellow, m. p. 247—249° (red melt) (Found: N, 5·4; Cl, 42·5. $C_{16}H_6O_4N_2Cl_6$ requires N, 5·6; Cl, 42·35%).

The filtrate from the above reaction mixture after removal of 1-nitro-3 : 6-bistrichloroacetylcarbazole gave with water a nearly colourless precipitate, which turned scarlet when treated with any of the usual solvents. When boiled with glacial acetic acid, it gave nitrous fumes (possibly from the >N·NO group) and, exposed to air, the scarlet solution deposited a red solid continuously during several months. Recrystallised, this gave scarlet nodules, m. p. 220—237° (Found: C, 38·9; H, 1·6; N, 6·4%). It dissolved in boiling potassium hydroxide solution. Addition of acetic acid and crystallisation of the precipitate from pyridine diluted with a small amount of water gave ill-defined crystals, unmelted at 300° (Found: N, 12·9. $C_{14}H_7O_7N_3$ requires N, 12·8%).

1-*Nitrocarbazole*-3 : 6-*dicarboxylic acid*. 1-Nitro-3 : 6-bistrichloroacetylcarbazole was boiled with excess of dilute potassium hydroxide solution until no more chloroform was evolved. The deep scarlet solution, treated hot with excess of hot glacial acetic acid, gave a canary-yellow precipitate, which separated from acetic anhydride in yellow micro-crystals of 1-*nitrocarbazole*-3 : 6-*dicarboxylic acid*, m. p. >300° (yield, 100%) (Found for a sample dried at 120°/1 hour: C, 55·9; H, 2·8; N, 9·2. $C_{14}H_8O_8N_2$ requires C, 56·0; H, 2·7; N, 9·3%).

1-*Nitrocarbazole*. 1-Nitrocarbazole-3 : 6-dicarboxylic acid (3·5 g.) was boiled with pure quinoline (35 ml.) and copper bronze (0·1 g.) for 2 hours. The mixture was steam-distilled to remove quinoline, and the black residue ground, boiled with dilute hydrochloric acid, washed with water, and extracted with aqueous ammonia to remove unchanged acid (0·05 g.). A benzene extract of the insoluble residue was passed through alumina (5 cm.) and eluted with benzene to give 1-nitrocarbazole, m. p. and mixed m. p. 187° (0·94 g.; yield, 38%). Charring occurred when 1-nitrocarbazole-3 : 6-dicarboxylic acid was heated alone. Attempts to remove quinoline by means of dilute acid, without steam-distillation, resulted in complete loss of 1-nitrocarbazole.

Ethyl Carbazole-3 : 6-*dicarboxylate*.—3 : 6-Bistrichloroacetylcarbazole (2 g.) was mixed with absolute ethanol (6 ml.) and a solution of sodium (0·1 g.) in absolute ethanol (4 ml.), occasionally shaken, and left for 5 hours (better, 2—3 days). The usual procedure gave carbazole-3 : 6-dicarboxylic acid (0·15 g.; yield, 13%) and pale cream prisms (from toluene–charcoal) of ethyl carbazole-3 : 6-dicarboxylate; the m. p. of the latter and that of a mixture with material prepared by esterifying carbazole-3 : 6-dicarboxylic acid (Dunlop and Tucker, *loc. cit.*, p. 1955) was 206° (corr.) (0·9 g.; yield, 67%).

Similarly, 3-trichloroacetylcarbazole gave ethyl carbazole-3-carboxylate, which, crystallised from ethanol, had m. p. and mixed m. p. 165—167° (yield, 80%).

Ethyl 1-*Nitrocarbazole*-3 : 6-*dicarboxylate*.—Ethyl carbazole-3 : 6-dicarboxylate (7 g.), dissolved in glacial acetic acid (100 ml.), was cooled to room temperature, a solution of concentrated nitric acid (15 ml.) in glacial acetic acid (20 ml.) added all at once, and the mixture left for 15 minutes, heated to the b. p., and filtered after standing. The crystalline precipitate, washed with very dilute aqueous ammonia and dried, gave *ethyl* 1-*nitrocarbazole*-3 : 6-*dicarboxylate*, which separated from acetic anhydride in yellow micro-crystals, m. p. 257—261°. The filtrate, treated with water, gave material which, when boiled with acetic anhydride, gave a copious evolution of nitrous fumes and, on cooling, a further crop of the above (total 7·1 g.; yield, 90%) (Found: C, 60·9; H, 4·4; N, 7·9. $C_{18}H_{16}O_8N_2$ requires C, 60·7; H, 4·5; N, 7·9%).

Hydrolysis of this ester was readily effected by boiling (5 mins.) with alcoholic-aqueous potassium hydroxide solution. Addition of hot glacial acetic acid gave 1-nitrocarbazole-3 : 6-dicarboxylic acid, m. p. >300° (6 g.; yield, 100%). Decarboxylation of this material gave 1-nitrocarbazole.

The following reference compounds were also prepared.

9-Toluene-*p*-sulphonylcarbazole (cf. Stevens and Tucker, J., 1923, **123**, 2147) was prepared free from carbazole thus: Carbazole (20 g.), toluene-*p*-sulphonyl chloride (40 g.), and acetone (200 ml.) were warmed to effect solution, and potassium hydroxide powder (33 g.) added. After precipitation by water and crystallisation from ethanol the product (23 g.) was suspended in glacial acetic acid (120 ml.), concentrated nitric acid (10 ml.) added, and the mixture shaken for 1 minute and poured into a large volume of water. The green precipitate, extracted with and crystallised from ethanol (charcoal), gave 9-toluene-*p*-sulphonylcarbazole (7 g.), m. p. 127—128°.

3-*Nitro*-9-*toluene*-p-*sulphonylcarbazole*. A mixture of 3-nitrocarbazole (2 g.), toluene-*p*-sulphonyl chloride (2 g.), and potassium hydroxide powder (1 g.) in acetone (20 ml.) was shaken for 10 minutes on the boiling water-bath and then poured into water. The precipitate crystallised from glacial acetic acid in yellow needles. Recrystallisation from glycol methyl ether gave colourless crystals of 3-*nitro*-9-*toluene*-p-*sulphonylcarbazole* (2·3 g.), m. p. 208—211° (yield, 65%) Found: C, 62·1; H, 3·8; N, 7·7. $C_{19}H_{14}O_4N_2S$ requires C, 62·3; H, 3·8; N, 7·7%).

An attempt to prepare the corresponding derivative of 1-nitrocarbazole failed.

9-(2'-Nitrotoluene-4'-sulphonyl)carbazole, prepared as above, 2-nitrotoluene-4-sulphonyl chloride being used, crystallised from alcohol in colourless needles, m. p. 164° (yield, 33%) (Found: N, 7·7. $C_{19}H_{14}O_4N_2S$ requires N, 7·7%).

The syntheses of 3-acetyl- and 3-cyano-carbazole and all the micro-analyses were carried out by Mr. J. M. L. Cameron. We thank the Carnegie Trustees for the award of a Research Scholarship (to R. W. G. P.).

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91. *The Preparation of 1-Substituted Carbazoles.*

By NEIL CAMPBELL and J. A. R. MACLEAN.

One successful and several unsuccessful attempts to prepare 1-substituted carbazoles are recorded. 3 : 6-Dibromo-1-aminocarbazole, when heated with concentrated hydriodic acid and red phosphorus, gives 1-aminocarbazole. *7-Bromo-1-phenylbenztriazole-5-carboxylic acid* loses bromine during the Graebe–Ullmann reaction to give carbazole. 9-Acetylcarbazole, when nitrated with Menke's reagent, gave little or no 1-nitrocarbazole and oxidation of 1-methylcarbazole yielded alkali-insoluble products which are probably dicarbazyls.

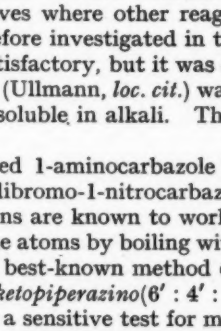
Mecke's reagent (selenious acid in sulphuric acid) is not specific for phenols, as it gives colorations also with diphenylamine, carbazole, and their derivatives.

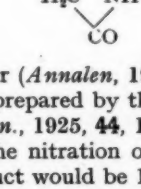
The bromocarbazoles show characteristic orange fluorescence.

THE preparation of 1-substituted carbazoles is difficult. Ullmann (*Annalen*, 1904, **332**, 84) obtained 1-methylcarbazole by the Graebe–Ullmann synthesis and Lindemann and Wessel (*Ber.*, 1925, **58**, 1221) prepared 1-aminocarbazole by a tedious process. This compound is obtained in good yield from 1-nitrocarbazole (Lindemann and Werther, *Ber.*, 1924, **57**, 1316), but the latter is obtained in poor yield by the nitration of carbazole (Lindemann, *ibid.*, p. 555; Morgan, J., 1931, 3283). Carbazole-1-carboxylic acid has been prepared (Ciamician and Silber, *Gazzetta*, 1882, **12**, 272; cf. Briscoe and Plant, J., 1928, 1990) with much loss in yield during purification. Gilman (*J. Org. Chem.*, 1937, **1**, 146) prepared the same acid by metalation. Other attempts to prepare 1-substituted carbazoles have been unsuccessful, Plant and Tomlinson (J., 1928, 2188), for example, failing to obtain 1-benzoylcarbazole by the Graebe–Ullmann synthesis. The present paper gives an account of attempts to find methods for preparing 1-substituted carbazoles.

3 : 4-Dibromo-5-nitrotoluene did not condense with aniline to give the required diphenylamine, the methyl group in the *p*-position apparently decreasing the reactivity of the 4-bromo-group. A similar effect has been noted with other bromonitrotoluenes (Lindemann and Pabst, *Annalen*, 1928, **462**, 24; Campbell, Anderson, and Gilmore, J., 1940, 446). The methyl group was therefore oxidised to carboxyl: the resulting acid condensed readily with aniline to give *2-bromo-6-nitrodiphenylamine-4-carboxylic acid* (cf. Schöpf, *Ber.*, 1889, **22**, 3281), from which *7-bromo-1-phenylbenztriazole-5-carboxylic acid* (I) was prepared. This compound, when heated at 360° with quicklime, yielded carbazole and not the expected 1-bromocarbazole.

(I.)





(II.)

The Graebe–Ullmann method has therefore certain limitations. Bremer (*Annalen*, 1934, **514**, 279) also noted this, though he indicated that monosubstituted carbazoles are readily prepared by the method.

It is well known that nitration with Menke's reagent (*Rec. Trav. chim.*, 1925, **44**, 141, 269) frequently gives *o*-substituted derivatives where other reagents give *p*-compounds. The nitration of 9-acetylcarbazole with this reagent was therefore investigated in the hope that the main product would be 1-nitro-9-acetylcarbazole. The results were unsatisfactory, but it was established that the yield of 1-nitrocarbazole was small.

1-Methylcarbazole (Ullmann, *loc. cit.*) was oxidised with various agents, but no carboxylic acid was obtained, the products being insoluble in alkali. They are probably dicarbazyls (cf. Tucker and Perkin, J., 1921, **119**, 217).

Finally we prepared 1-aminocarbazole by the following series of reactions: Carbazole ⟶ 3 : 6-dibromocarbazole ⟶ 3 : 6-dibromo-1-nitrocarbazole ⟶ 3 : 6-dibromo-1-aminocarbazole ⟶ 1-aminocarbazole. The first three reactions are known to work smoothly (Lindemann and Mühlhaus, *Ber.*, 1925, **58**, 2371). The removal of the bromine atoms by boiling with concentrated hydriodic acid gave a 35% yield of 1-aminocarbazole and thus afforded the best-known method of obtaining this compound. The compound was characterised by the preparation of *2'-ketopiperazino(6' : 4' : 1 : 9)carbazole* (II).

Mecke's reagent is a sensitive test for many alkaloids, but Levine's statement (*Centr.*, 1926, II, 925) that it is specific for phenolic compounds is incorrect, for it gives colorations with many derivatives of diphenylamine, carbazole, etc. The colorations are also obtained if selenic acid is substituted for selenious acid.

The fluorescence of the bromocarbazoles may be used for their detection and identification, brilliant orange fluorescence being observed in ultra-violet light.

Experimental.

Unless otherwise stated, the preparation, properties, and purification of compounds used are those given in the literature. M. p.'s were determined in Kofler's apparatus (*Mikrochem.*, 1934, **15**, 242) and analyses were done by Drs. Weiler and Strauss, Oxford. Fluorescence observations were made with ultra-violet light from a Hanovia mercury lamp provided with a filter to eliminate visible waves.

Attempted Preparation of 2-Bromo-6-nitro-4-methyldiphenylamine.—3 : 4-Dibromo-5-nitrotoluene (Cohen and Dutt, J., 1914, **105**, 510) was treated under different conditions with aniline, but even in the presence of copper bronze or anhydrous sodium acetate no condensation products were obtained. That the 4-bromo-group is not completely inactive was shown by heating the compound with piperidine at 50° for 2 hours; on cooling, yellow plates of piperidine hydrobromide, m. p. 210—225°, separated.

2-Bromo-6-nitrodiphenylamine-4-carboxylic Acid.—3 : 4-Dibromo-5-nitrotoluene (60 g.) and nitric acid (*d* 1·2; 1450 c.c.) were refluxed for 24 hours. The solution, when cooled, deposited a solid, which was shaken with sodium hydroxide solution; after filtration, the liquid was acidified with concentrated hydrochloric acid. Crystallisation from boiling water yielded 20 g. (30%) of 3 : 4-dibromo-5-nitrobenzoic acid in needles, m. p. 180—182° (lit., 183°). Other methods of oxidation gave less satisfactory results. The acid was heated over a naked flame with excess of aniline for 40 minutes. Concentrated hydrochloric acid was then added, and the mixture poured into water. *2-Bromo-6-nitrodiphenylamine-4-carboxylic acid* was obtained in golden-yellow crystals from benzene, m. p. 207—208°. It sublimed in lustrous plates (Found : C, 46·3; H, 2·8; Br, 23·7. $C_{13}H_9O_4N_2Br$ requires C, 46·3; H, 2·7; Br, 23·7%). The *methyl* ester, obtained in similar manner from methyl 3 : 4-dibromo-5-nitrobenzoate, formed light brown prisms, m. p. 151—152°, from benzene (Found : N, 8·4. $C_{14}H_{11}O_4N_2Br$ requires N, 8·0%).

7-Bromo-1-phenylbenztriazole-5-carboxylic Acid.—The preceding acid (6 g.) was heated for 24 hours on a water-bath with crystalline sodium sulphide (18 g.) and water (25 c.c.). Glacial acetic acid gave a precipitate, which was shaken with warm sodium carbonate solution; after filtration to remove sulphur, acidification with glacial acetic acid yielded *2-bromo-6-aminodiphenylamine-4-carboxylic acid*, which was crystallised from alcohol; m. p. 244—245°. It sublimed in colourless plates (Found : N, 9·2. $C_{13}H_{11}O_2N_2Br$ requires N, 9·1%). Yield, 4·5 g. (80%). The *acetyl* derivative, prepared by shaking the compound (0·2 g.) with water (1 c.c.) and acetic anhydride (12 drops) for 15 minutes, crystallised from methyl alcohol in white needles, m. p. 163—164° (Found : N, 8·2. $C_{15}H_{13}O_3N_2Br$ requires N, 8·0%). The amino-compound (4·5 g.) was dissolved in water (50 c.c.) containing sodium carbonate (1·8 g.) and, after slow addition of sodium nitrite (2·3 g.) in the minimum amount of water, was added drop by drop to well-stirred sulphuric acid (10%). Stirring was continued for 15 minutes, and the solution then kept at room temperature for 2 hours. *7-Bromo-1-phenylbenztriazole-5-carboxylic acid* separated and was obtained in almost quantitative yield from aqueous methyl alcohol, m. p. 215—217°. It sublimed in colourless needles or cubes (Found : N, 13·3. $C_{13}H_8O_2N_3Br$ requires N, 13·2%).

Graebe–Ullmann Reaction with 7-Bromo-1-phenylbenztriazole-5-carboxylic Acid.—The triazole (1·5 g.) was ground with freshly prepared quicklime (3 g.) and heated in a distilling flask to 360°. Micro-extraction of the sublimate and oily distillate yielded a light brown compound (0·1 g.), m. p. 220—230°, which did not contain bromine and proved to be carbazole (violet fluorescence; deep green colour with sulphuric acid and a trace of nitric acid; mixed m. p.).

2-Chloro-2′-nitrodiphenylamine.—*o*-Bromonitrobenzene (3 g.) was heated with excess of *o*-chloroaniline, potassium carbonate (1 g.), and a trace of copper bronze at 160—170° for 15 hours. The mixture was extracted with concentrated hydrochloric acid, and the residue with light petroleum (b. p. 100—120°). *2-Chloro-2′-nitrodiphenylamine* separated and was obtained in red prisms, m. p. 114°, from alcohol; yield, 1·1 g. (20%) (Found : C, 58·1; H, 3·5. $C_{12}H_9O_2N_2Cl$ requires C, 57·9; H, 3·6%).

1-Aminocarbazole.—3 : 6-Dibromo-1-aminocarbazole was obtained in 54% yield from 3 : 6-dibromo-1-nitrocarbazole (Lindemann and Mühlhaus, *loc. cit.*, give no yield). The acetyl compound sublimed in white lustrous plates, m. p. 262—264° (Found : N, 7·3. Calc. for $C_{14}H_{10}ON_2Br_2$: N, 7·3%). Lindemann and Mühlhaus (*loc. cit.*) did not give a m. p.

3 : 6-Dibromo-1-aminocarbazole (10 g.) was refluxed for 4 hours with hydriodic acid (*d* 1·94; 40 g.) and red phosphorus (3·5 g.), boiling water (25 c.c.) added, and the liquid filtered hot. The filtrate was treated until neutral with a saturated solution of sodium acetate, and the resulting 1-aminocarbazole crystallised from benzene, giving colourless needles, m. p. 193—195° (lit., 195°). Yield, 1·7 g. (30%) (Found : N, 15·3. Calc. for $C_{12}H_{10}N_2$: N, 15·4%).

2′-Ketopiperazino(6′ : 4′ : 1 : 9)carbazole.—1-Aminocarbazole (1·0 g.) in benzene (25 c.c.) was refluxed with bromoacetyl bromide (0·5 c.c.) in benzene (5 c.c.) for 30—35 minutes, and the solution kept overnight; it was then filtered and evaporated to half volume in a vacuum at room temperature. *1-ω-Bromoacetamidocarbazole* was obtained in colourless or pale green prisms, m. p. 188° (Found : Br, 26·1. $C_{14}H_{11}ON_2Br$ requires Br, 26·4%). 1-ω-Bromoacetamidocarbazole (0·5 g.), ethyl alcohol (100 c.c.), and 50% aqueous potassium hydroxide (1 c.c.) were refluxed for 30 minutes, and the solution kept overnight and then poured into 50 c.c. of concentrated hydrochloric acid. The precipitate was triturated with water and then with methyl alcohol and crystallised from xylene; it had m. p. 255°, subliming in colourless prisms. Yield, poor (Found : N, 12·0. $C_{14}H_{10}ON_2$ requires N, 12·5%).

Bromocarbazoles and Hydriodic Acid.—3 : 6-Dibromocarbazole (4 g.), hydriodic acid (*d* 1·94; 20 c.c.), and red phosphorus (1 g.) were refluxed for 4 hours, and the mixture poured into potassium iodide solution. The precipitate was extracted with alcohol and yielded carbazole (1·2 g.), m. p. and mixed m. p. 239°. The same result was obtained with 1 : 3 : 6-tribromo- and 3 : 6-di-iodo-carbazole.

Bromocarbazoles and Stannous Chloride–Hydrochloric Acid.—3 : 6-Dibromocarbazole (4 g.), glacial acetic acid (50 c.c.), concentrated hydrochloric acid (20 c.c.), and stannous chloride (4·7 g.) were refluxed for 3 hours. A quantitative yield of carbazole, m. p. 240°, was obtained. 1 : 3 : 6-Tribromocarbazole (4 g.) was not attacked under these conditions, but after 48 hours' refluxing, carbazole (0·1 g.) was isolated, most of the original compound being recovered.

Selenious Acid Colorations.—The following colorations were obtained with Mecke's reagent: Pyrrole, brown; indole, magenta → green (heat); diphenylamine, blue (heat); 2-aminodiphenylamine, magenta; 2-nitrodiphenylamine, violet; triphenylamine, cobalt-blue; carbazole, 1-methylcarbazole, 1-aminocarbazole, and 3 : 6-dibromocarbazole, dark green; 3 : 6-di-iodocarbazole, bluish-green; tribromocarbazole and tetrabromocarbazole, none. Magenta colorations were also obtained with several substituted *o*-amino- and *o*-nitro-diphenylamines. No colours were obtained with pyridine, 2-phenylindole, and indazole.

Fluorescence of Substituted Carbazoles.—In the crystalline state the bromocarbazoles have characteristic fluorescence which offers a ready means of detection and identification. 3 : 6-Dibromo- (yellowish-orange), 1 : 3 : 6-tribromo- (reddish-orange), 1 : 3 : 6 : 8-tetrabromo-carbazole (deep orange-red).

We wish to thank the Moray Fund for a grant.

University of Edinburgh.

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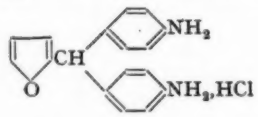
92. *Reactions of Furan Compounds. Part I. Constitution of the Coloured Condensation Product from Furfural, Aniline, and Aniline Hydrochloride.*

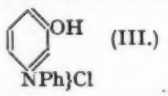
By Gerald Williams and Christopher L. Wilson.

The evidence for the structure of the condensation product from furfural, aniline, and aniline hydrochloride is summarised and discussed. It has been shown that reaction with nitrous acid liberates aniline. Subsequent coupling reactions produce benzeneazo-derivatives. This demonstration would appear to discredit recent conclusions by Riegel and Hathaway (*J. Amer. Chem. Soc.*, 1941, **63**, 1835) in favour of a triphenylmethane structure (I). The glutaconic dialdehyde structure (II) is still, therefore, to be preferred.

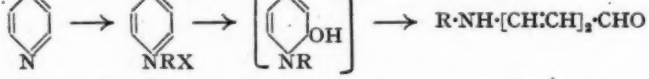
When furfural, aniline, and aniline hydrochloride are mixed in equimolecular amounts in alcoholic solution, a deeply coloured condensation product rapidly crystallises. After purification the material forms prismatic crystals, almost like potassium permanganate in appearance, melts at 166—167° (decomp.), and gives the analytical figures required for a hydrochloride, $C_{17}H_{16}ON_2$,HCl. Schiff (*Annalen*, 1880, **201**, 355; 1887, **239**, 349) thought the substance had a triphenylmethane structure (I), but later investigators (Zincke and Mülhausen, *Ber.*, 1905, **38**, 3824; König, *J. pr. Chem.*, 1905, **72**, 555; Dieckmann and Beck, *Ber.*, 1905, **38**, 4122) preferred an open-chain representation (II), based on glutaconic dialdehyde. The reasons for this change were briefly as follows: the substance readily loses a molecule of aniline on heating to give 3-hydroxy-1-phenylpyridinium chloride (III), a reaction which would necessitate a simple cyclisation of (II) but a complex rearrangment of (I). Further support for (II) is afforded by the similarity in properties, particularly colour, between the furfural

(I.) 

Ph·NH·CH:CH·CH:C(OH)·CH:NPh,HCl (II.)

 (III.)

derivative and a series of compounds obtainable from pyridine for which a glutaconic dialdehyde structure is generally assumed. These reactions comprise the addition of molecules such as 2 : 4-dinitrochlorobenzene (Zincke, *Annalen*, 1903, **330**, 361; 1904, **333**, 296; **338**, 107; 1905, **341**, 365; 1915, **408**, 285), cyanogen bromide (König, *J. pr. Chem.*, 1904, **69**, 105; **70**, 19; 1911, **83**, 406), phosphorus pentachloride (Reitzenstein and Breuning, *J. pr. Chem.*, 1911, **83**, 97), or ethyl chlorosulphonate (Baumgarten, *Ber.*, 1924, **57**, 1622; 1925, **58**, 2018; 1926, **59**, 11) to pyridine to produce, most probably, a type of quaternary salt, which, on treatment with alkali or aniline, gives derivatives of glutaconic dialdehyde. The reaction may be represented by the following formulæ, which, in part, recall the behaviour of a ψ-base such as cotarnine:



Baumgarten (*loc. cit.*) has shown that the reverse process to give pyridine may be realised and has thus provided an interesting analogy for the reaction (II) ⟶ (III).

There is much more evidence of a similar nature which, although indirect, supports (II). It was, therefore, with considerable interest that we noticed that Riegel and Hathaway (*loc. cit.*) have recently concluded that, in spite of previous evidence, the triphenylmethane structure (I) is most probably correct. In the present paper we wish to reinterpret the evidence presented by these authors.

Riegel and Hathaway's contention was based essentially on the observation that the furfural product reacted with nitrous acid (2 equivs.), giving a solution of a diazonium salt which could be coupled with hydroxy- and amino-naphthalenesulphonic acids and the like to produce wool dyes. These compounds were analysed, but only for nitrogen, and the figures were shown to compare favourably with those required for bisazo-compounds derived from (I). We have repeated these experiments and have shown that the condensation product does indeed react with nitrite as R. and H. say. The resulting solution, however, on reaction with β-naphthol (not investigated by R. and H.) produces benzeneazo-β-naphthol. Identity was shown by analysis and mixed melting point with an authentic specimen. In the reaction with nitrous acid it appears, therefore, that aniline is liberated. Further confirmation was provided by analogous experiments with the condensation product of furfural and *p*-toluidine, which gave tolueneazo-β-naphthol. Fission of aniline from (II) is not surprising in view of the known sensitivity of Schiff's bases towards acids. We have also shown that aniline is liberated by reaction of the furfural derivative with aqueous sodium bisulphite. The fate of the remainder of the molecule in these two reactions is not known.

Having disposed of the main difficulty, we are now in a position to deal with the rest of Riegel and Hathaway's argument. Viewed impartially, most of this really supports (II). For instance, their reaction scheme for the conversion of (I) into (III) is so highly imaginative as to condemn it; the failure to bring about reaction between furfural, dimethylaniline, and dimethylaniline hydrochloride in alcoholic solution suggests that a primary amino-group and not a reactive *p*-position is essential for the condensation; and lastly, their reference, in order to illustrate the stability of the furan ring, to the formation (Renshaw and Naylor, *J. Amer. Chem. Soc.*, 1922, **44**, 862; Mahood and Harris, *ibid.*, 1924, **46**, 2810; Mahood and Aldrich, 1930, **52**, 4477) of a true

malachite-green analogue by reaction between furfural and dimethylaniline under the influence of zinc chloride, followed by oxidation with lead dioxide, serves only to stress the improbability of (I) being formed under milder conditions in the absence of zinc chloride. Furthermore it would be surprising if (I), which is a leuco-compound, possessed much colour at all, and it is interesting that Renshaw and Naylor (*loc. cit.*) have demonstrated that the *NN'*-tetramethyl derivative of (I) is only faintly yellow.

Riegel and Hathaway, by the reaction between furfural, dimethylaniline, and aniline hydrochloride, obtained a coloured condensation product which they considered to be an *N*-dimethyl derivative of (I). We have repeated this reaction and have been able to isolate only small amounts of the simple unmethylated compound derived from furfural, aniline, and aniline hydrochloride.

So far we have ignored the table of nitrogen analyses recorded by Riegel and Hathaway for the wool dyes referred to above. It does not seem possible to assume that these were simple benzeneazo-derivatives, since the latter would require nitrogen figures which are up to 1 unit higher than those listed. Nevertheless we think that nitrogen analyses on complex dyes, which are notoriously difficult to purify, are hardly sound criteria to apply in the present connection. In the case of α-naphthol (recorded in R. and H.'s list) we have shown that the product from both diazotised aniline and the furfural compound is a complex mixture, as is frequently the case with α-naphthol as second diazo-component. We have also been able to show, by spotting on filter-paper, that, if the solutions are equally concentrated, the colours produced, as well as the shade changes caused by acid and alkali treatment afterwards, in the coupling reactions tabulated by Riegel and Hathaway are remarkably similar to those given by the simple benzeneazo-compounds.

With this material before us we think the balance of evidence is strongly in favour of (II).

Experimental.

The Condensation Product.—An almost quantitative yield was obtained by mixing redistilled furfural (21 c.c.; 0·25 mol.) and aniline (45·5 c.c.; 0·5 mol.) in ethyl alcohol (150 c.c.) and adding 10N-hydrochloric acid (25 c.c.; 0·25 mol.) in ethyl alcohol (25 c.c.). Recrystallisation from glacial acetic acid gave small, almost black, prisms which, after drying in a vacuum, had m. p. 166—167° (decomp.) (Found: C, 67·7; H, 5·9. Calc. for $C_{17}H_{16}ON_2,HCl$: C, 67·8; H, 5·65%).

Reaction with Nitrous Acid.—The above compound (3·05 g.; 0·01 mol.) was suspended in ethyl alcohol (200 c.c.), concentrated hydrochloric acid (2 c.c.) added, and the mixture cooled in ice while N-sodium nitrite was run in and more acid added from time to time to maintain acidity to Congo-red. An immediate positive starch–iodide reaction was obtained only after much more than two equivalents of nitrite had been added. The solution was rapidly filtered to remove the suspended brown solid material.

Coupling with β-Naphthol.—The diazonium solution obtained above was added to β-naphthol dissolved in excess of 2N-sodium hydroxide. The solid obtained corresponded in amount to slightly less than one mol.-equiv. of aniline; recrystallised from petrol (b. p. 60—80°), it formed red needles, m. p. 130—131° (Found: C, 77·35; H, 5·0; N, 11·6. Calc. for $C_{16}H_{12}ON_2$: C, 77·3; H, 4·8; N, 11·3%), not depressed by the product from benzenediazonium chloride and β-naphthol (m. p. 130—131°).

A similar result was obtained, although purification of the product was rendered more difficult by the presence of other substances, when exactly 2 equivs. of sodium nitrite were added in the original diazotisation.

Coupling with α-Naphthol.—The diazonium solution both from the furfural product and from aniline gave a mixture of substances. From the former, after recrystallisation from butyl acetate, a small amount of a product, m. p. 178° (decomp.) (Found: C, 70·45; H, 4·25; N, 10·85%), was obtained. Riegel and Hathaway give a nitrogen figure of 9·91%. Their calculated figure (10·22%) would appear to be in error; we find 9·76%. The triphenylmethane structure (I) would necessitate C, 77·3; H, 4·6% for the bisazo-derivative.

Coupling Products from the Toluidine Condensation Product.—The procedure was as described for aniline. The condensation product after recrystallisation from glacial acetic acid formed almost black prisms with a bluish-grey reflex, m. p. 159—161° (decomp.) (Found: C, 69·1; H, 6·8; N, 8·35. Calc. for $C_{19}H_{20}ON_2,HCl$: C, 69·4; H, 6·4; N, 8·5%). After coupling with β-naphthol the product separated from petrol (b. p. 60—80°) in red needles, m. p. 130—131° (Found: C, 77·55; H, 5·75; N, 10·7. Calc. for $C_{17}H_{14}ON_2$: C, 77·8; H, 5·4; N, 10·7%). The substance did not depress the m. p. of an authentic specimen from diazotised *p*-toluidine and β-naphthol. It did, however, depress the m. p. of benzeneazo-β-naphthol, which has the same m. p.

Reaction of Dimethylaniline, Aniline Hydrochloride, and Furfural.—Equimolecular amounts of the reactants were mixed in methyl alcohol. After some time a small amount of crystalline material had separated. Recrystallisation from glacial acetic acid gave almost black prisms, m. p. 166—167° (decomp.), not depressed by the aniline–aniline hydrochloride product. Identity was further supported by analysis (Found: C, 68·35; H, 6·0. Calc. for $C_{17}H_{16}ON_2,HCl$: C, 67·8; H, 5·65%. Calc. for $C_{19}H_{20}ON_2,HCl$: C, 69·4; H, 6·4%).

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93. *Sophora Alkaloids. Part III. The Alkaloids of the Seeds of* S. chrysophylla.

By Lindsay H. Briggs and William E. Russell.

The alkaloids from the seeds of *Sophora chrysophylla* are shown to consist chiefly of cytisine and anagyrine with a third base in small quantity probably identical with an unidentified base isolated from *S. microphylla* and *S. tetraptera*, for which the name sophochrysine is suggested.

Sophora chrysophylla (native name, "Mamami") is an inland species endemic to Hawaii, resembling the New Zealand "Kowhai" (*S. microphylla*). The alkaloids from the seeds have been isolated and examined by methods similar to those described in Parts I and II (J., 1937, 1795; 1938, 1206). The distilled alkaloids from

the mixture of crude bases (yield, *ca.* 2%) have been separated by fractional crystallisation of the free bases and their salts and shown to consist mainly of cytisine and anagyrine in the approximate proportion of 1 : 4. *S. chrysophylla* therefore resembles *Anagyris fœtida*, which contains the same alkaloids (Ing, J., 1943, 504; Partheil and Spasski, *Apoth.-Ztg.*, 1895, **10**, 903). From material insoluble in acetone, a third base, m. p. 284—287°, has been isolated. Although it could not be obtained crystalline, it formed a crystalline aurichloride, m. p. 190—192° (decomp.), picrate, m. p. above 360°, and a picrolonate, m. p. 255—258° (decomp.). This base is, in our opinion, identical both with base D, from *S. microphylla* (cf. Part I), which has m. p. 293—296° (picrate, m. p. above 350°, and picrolonate, m. p. 261° with sintering at 257—258°), and with a third base from *S. tetraptera* (cf. Part II), which gave a crystalline aurichloride, m. p. 186° (decomp.), although direct comparisons could not be made owing to the minute amounts of alkaloid separated from *S. microphylla* and *S. tetraptera*. All three bases were obtained from fractions insoluble in light petroleum, and the first two bases had similar solubilities and failed to give the van der Moer reaction. We suggest the name sophochrysine for this new alkaloid (cf. also Part IV to follow). Analyses of the *picrate* and *picrolonate* did not confirm the original formula suggested, $C_{15}H_{23}O_4N_3$, but the analytical data are still too meagre for a definite formula, a more probable decision lying between $C_{13-15}H_{21-19}O_2N_3$.

Experimental.

3·22 Kg. of the seeds of *S. chrysophylla* were worked up as described in Part II, yielding after 18 days of continuous extraction with trichloroethylene 60 g. of a dark brown, viscous oil (K), (yield, *ca.* 2%). Since basic material still remained in the aqueous solution, extraction was continued with chloroform for 15 days, giving a further 4 g. of deep red, hygroscopic material (L). Since even this treatment failed to extract all the basic material, precipitation of the remaining alkaloids was brought about by the addition of Mayer's reagent, 3·3 g. of dark amorphous material (M) being recovered. Fractions L and M gave positive tests for nitrogen and pyrrole bases on dry distillation (pine shaving test), but no crystalline material could be obtained as a free base or as a salt and fraction L could not be distilled in low vacuum without decomposition.

Distillation of (K) gave a product (35 g.), b. p. 192—195°/0·15 mm., solidifying to a yellowish-brown glassy solid containing some crystalline material. The residue (N) in the neck of the flask was worked up later. The distilled alkaloids were again distilled and collected in two fractions: (*a*) 21·31 g., b. p. 175—180°/0·1—0·2 mm., and (*b*) 8·61 g., b. p. 200—215° (mainly 207°)/0·1 mm. The first fraction partly crystallised on standing while the second fraction remained as a clear glass.

18% of fraction (*a*) was obtained crystalline by treatment with acetone, followed by recrystallisation from benzene and light petroleum (b. p. 80—100°), to give a pure base A, m. p. 153·5—154·5°. No other crystalline base could be obtained from the mother-liquors, but 50% of another base B could be obtained as the picrate, m. p. 243—244·5° (decomp.).

Fraction (*b*) did not yield base A, but mainly dissolved in acetone, leaving an amorphous residue of base C, m. p. 284—287° after darkening at *ca.* 228° (yield, 220 mg. from 6·68 g.).

From another aliquot portion, 76% of base B could be obtained as the perchlorate, m. p. 292° (decomp.).

Base A.—This base has been identified as cytisine by mixed m. p. determinations with authentic specimens of the free bases and their derivatives (Found: C, 69·3; H, 7·3. Calc. for $C_{11}H_{14}ON_2$: C, 69·4; H, 7·4%). $[\alpha]_D^{25°}$ − 114·6° ($l = 1$, $c = 0·8460$ in water). Partheil (*Arch. Pharm.*, 1892, **230**, 448) records $[\alpha]_D^{25°}$ − 119·5°. The m. p.'s of the base and its derivatives compared with recorded values are as follows (for references, see Part I): base, m. p. 153·5—154·5° (150—156°); picrate, m. p. 277° (decomp.) (278°, decomp.); aurichloride, m. p. 218—220° (decomp.) (219°, decomp.); methiodide of methylcytisine, m. p. 271—275° (270—280°). Ing (J., 1933, 506) refers to a perchlorate but gives no m. p. The *perchlorate*, prepared by addition of 20% aqueous perchloric acid to the base in ethyl acetate, crystallised from alcohol in long colourless needles, m. p. 296° (decomp.) (Found: N, 9·6. $C_{11}H_{14}ON_2,HClO_4$ requires N, 9·8%). The picrolonate, prepared from the components in hot alcohol, crystallised from alcohol in bright yellow needles, m. p. 270° (decomp.) with sintering at 265°.

Base B.—This base has been identified as anagyrine. It gives a positive van de Moer test, is deliquescent, and is soluble in the common solvents except light petroleum, in which it is only slightly soluble. $[\alpha]_D^{25°}$ − 146·9° ($l = 1$, $c = 1·062$ in absolute alcohol). Ing (*loc. cit.*) records $[\alpha]_D^{25°}$ − 165·3° and Oréchov (*Ber.*, 1934, **67**, 1394) $[\alpha]_D^{25°}$ − 151·7°. In agreement with these workers we have not been successful in crystallising the base.

The picrate crystallised from water or alcohol in slender yellow needles, m. p. 243—244·5° (decomp.). Oréchov (*loc. cit.*) records m. p. 242—243° and Clemo and Raper (J., 1935, 10) m. p. 242° (Found: C, 53·2; H, 4·8. Calc. for $C_{15}H_{20}ON_2$: C, 53·25; H, 4·9%). $[\alpha]_D^{25°}$ − 145·7°. Clemo and Raper record $[\alpha]_D^{25°}$ − 148·5°.

The picrolonate crystallised from aqueous alcohol in yellow needles, m. p. 253° (decomp.). Clemo and Raper (*loc. cit.*) record m. p. 254° (decomp.).

The mercurichloride crystallised from aqueous alcohol in clusters of colourless needles, m. p. 221·5—224°, and on standing prisms separated, m. p. 230—232°. Litterscheid (*Arch. Pharm.*, 1900, **238**, 191) records three forms: (*a*) with water of recystallisation, m. p. 225—226°; (*b*) anhydrous, slender white needles, m. p. 213—214°; (*c*) white nodular crystals, m. p. 231°. Oréchov (*Ber.*, 1934, **67**, 1394), however, records only one form, m. p. 220—222°.

The methiodide, from the base (200 mg.) in methyl alcohol and methyl iodide (0·5 c.c.), separated in colourless needles after the mixture had been heated for an hour; after repeated crystallisation from methyl alcohol it had m. p. 262° (decomp.). Clemo and Raper (*loc. cit.*) record colourless plates, m. p. 264° (decomp.).

The perchlorate, which Ing (*loc. cit.*) recommends as the most convenient means of separation from cytisine, is described as colourless needles decomposing at 270° without melting. In this case the perchlorate, after recrystallisation from water containing a little ethyl acetate, formed colourless needles which darkened at 267° and decomposed at 298·5°.

Base C.—This base, sophochrysine, m. p. 284—287°, could not be crystallised. It is freely soluble in water, ethyl and methyl alcohol, sparingly soluble in benzene and chloroform, and insoluble in acetone, ethyl acetate and light petroleum. It does not give the van de Moer reaction. $[\alpha]_D^{25°}$ − 113·2° ($l = 1$, $c = 0·795$ in absolute alcohol). The *picrate*, formed on addition of alcoholic picric acid to an aqueous solution of the base (7 mg.), separated on cooling in short yellow needles which darkened at 250° but did not melt below 360° [Found: C, 47·9; H, 4·9; N, 17·1. $C_{13}H_{21}O_2N_3(?),C_6H_3O_7N_3$ requires C, 47·5; H, 5·0; N, 17·5%].

The *picrolonate*, prepared similarly from the base (13 mg.), after recrystallisation from water formed yellow needles, m. p. 265·5—267° (decomp.) [Found: C, 56·2; H, 4·8; N, 18·8. $C_{15}H_{19}O_2N_3(?),C_{10}H_8O_5N_4$ requires C, 55·9, H, 5·0; N, 18·3%].

The aurichloride, formed from the base (5 mg.) in the usual way, crystallised from dilute hydrochloric acid in clusters of bright yellow needles, m. p. 190—192° (decomp.). It was unsuitable for molecular weight estimations, as it darkened and decomposed on standing, but was apparently stable in suspension in the mother-liquors of the preparation.

The residue (N) from the first distillation of the bases was dissolved in water and aliquot portions were treated with picric acid and picrolonic acid. The former acid gave an amorphous picrate, m. p. 237° (decomp.), and, on standing, long yellow needles, m. p. 260° (decomp.). Both products, however, after crystallisation from water darkened at *ca.* 250° but did not melt below 360° and consisted apparently of sophochrysine picrate. From the latter acid an amorphous picrolonate was obtained which after crystallisation from aqueous alcohol had m. p. 260—261·5°, undepressed by sophochrysine picrolonate.

The analyses are by Dr. Burger.

We are greatly indebted to Mr. L. W. Bryan, of the Board of Commissioners of Agriculture and Forestry, Hawaii, for the whole of the generous supply of the seeds of *S. chrysophylla* and to the Chemical Society for a grant.

AUCKLAND UNIVERSITY COLLEGE, AUCKLAND, NEW ZEALAND. [*Received, April 23rd*, 1942.]

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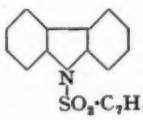
94. *The Nitration of* 9-p-*Toluenesulphonylcarbazole.*

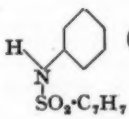
By B. K. MENON, E. V. MENON, and DAVID H. PEACOCK.

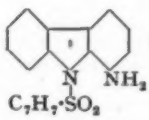
9-*p*-Toluenesulphonylcarbazole is nitrated in the 1-position apparently exclusively; bromination, however, occurs only in the 3-position and by the action of iodine monochloride only the 3 : 6-di-iodo-compound could be obtained. The 1-*nitro*-compound gave a mixture of two *dinitro*-compounds, neither of which was identical with the 3 : 6-*dinitro*-compound produced by nitration of 3-*nitro*-9-p-*toluenesulphonylcarbazole*. The resolution of the 1-amino-compound is being attempted.

THE nitration of 3-*nitro*-9-p-*toluenesulphonylcarbazole* gave the 3 : 6-*dinitro*-compound, and nitration of the 1-nitro-compound and dinitration of 9-*p*-toluenesulphonylcarbazole gave in each case a mixture of the same two compounds, which are probably the 1 : 6- and the 1 : 8-compound. 1-*Nitro*-9-p-*toluenesulphonylcarbazole* is nitrated much more readily than the 3-nitro-compound. Treatment of 9-*p*-toluenesulphonylcarbazole with sulphuric acid effected simultaneous sulphonation and hydrolysis of the *p*-toluenesulphonyl group; pyridine–sulphur trioxide gave similar results.

The 1-nitro-compound was hydrolysed with difficulty to 1-nitrocarbazole and this in turn was reduced to 1-aminocarbazole (Lindemann, *Ber.*, 1924, **57**, 1316; Morgan and Mitchell, J., 1931, 3284). On diazotisation a crystalline diazonium salt was obtained which did not give a triazole when treated with ammonia (Morgan and Mitchell, *loc. cit.*). 1-*Amino*-9-p-*toluenesulphonylcarbazole* (III) was obtained on reduction of the nitro-compound. If the three valencies of the ring nitrogen atom are not coplanar, the compound (III) should be capable of resolution.

(I.) 

(II.) 

(III.) 

The formation of the 1-nitro-derivative from (I) corresponds to the formation of an *o*-nitro-derivative from (II). Nitration in the *o*-position to an amino-group appears to be facilitated by the conversion of the amino-group into the *p*-toluenesulphonamido-group (Reverdin and Crépieux, *Ber.*, 1902, **35**, 1440; D.R.-P. 157,859 and 163,516), but in those cases where the *p*-position is free a mixture of the *o*- and the *p*-isomer is obtained. In the present instance no other isomer has been observed, although the 3-position is open to nitration and this is the position attacked by bromine and by iodine monochloride. In other cases where only one isomer has been obtained, the *p*-position, corresponding to the 3- and the 6-position in carbazole, has been occupied as in the *p*-toluenesulphonyl derivatives of *p*-toluidine (Reverdin and Crépieux, *loc. cit.*), 4-aminodiphenyl (Bell and Kenyon, J., 1926, 2708), and 4-methylaminodiphenyl (Bell and Robinson, J., 1927, 1129).

The toluenesulphonyl group is a strongly polar group and association with a polar reagent, such as nitric acid, may assist substitution in the adjacent positions as suggested by Lapworth and Robinson (*Mem. Manchester Phil. Soc.*, 1928, **72**, 43). In this connection it is noteworthy that bromine, a non-polar reagent, substitutes in the 3-position. On the other hand, iodine monochloride, a polar reagent, reacted in the 3- and the 6-position. Nitration in the 1-position seems to be bound up with the strong polarity of the sulphonyl group, as 9-benzoyl- and 9-acetyl-carbazole are nitrated in the 3-position.

The difference in behaviour of (I) and (II) may also be due to the restriction of rotation about the C–N–C bond in (I) as compared with the free rotation possible in (II). The inductive effect exerted by the sulphonyl group on positions 1 and 8 in (I) will therefore be greater than its effect on positions 2 and 6 in (II). It is hoped to study the nitration of similar compounds in which free rotation has been prevented.

Unsuccessful attempts to resolve the alkaloidal salts of 9-ethyl-, 9-methyl-, and 9-benzyl-carbazolesulphonic acid have been made (cf. Peacock, Dissert., London, 1927). The introduction of the sulphonyl group, by lowering the mesomeric effect of the nitrogen atom, may stabilise the dissymmetric forms and 1-amino-9-*p*-toluenesulphonylcarbazole is being examined. It has, however, been found that, in a somewhat similarly constituted

compound, 2-*m*-carboxybenzenesulphonyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, where mesomerism with an adjacent benzene ring is excluded, no active forms could be isolated (Peacock, unpublished results).

Experimental.

9-p-*Toluenesulphonylcarbazole*.—Carbazole (33·7 g.) was fused with potassium hydroxide (17 g.) at 230°, the powdered product mixed with solvent naphtha (200 c.c.), and the solvent distilled to remove water. The residue was mixed with *p*-toluenesulphonyl chloride (40 g.) in toluene (200 c.c.), left overnight, and then stirred at 140—150° for 6 hours. After cooling, the solid was collected and washed with toluene and the combined toluene solutions were steam-distilled. The residue, after crystallisation from rectified spirit, had m. p. 137—138° (40 g.) (D.R.-P. 224,951; Stevens and Tucker, J., 1923, **123**, 2140). The solid was boiled with water and left 10 g. of carbazole.

1-*Nitro*-9-p-*toluenesulphonylcarbazole*.—A solution of the preceding compound in glacial acetic acid (300 c.c.) at 60° was treated with 98% nitric acid (12·0 g.), added during ½ hour, and then allowed to cool after 6 hours' stirring. The crystalline solid (38 g.) was collected, and the filtrate poured into ice-water, giving a further crop (14·0 g.). The combined crops, crystallised from glacial acetic acid, had m. p. 134°; yield, 45 g. (Found : N, 7·3. $C_{19}H_{14}O_4N_2S$ requires N, 7·65%).

1-*Nitrocarbazole*.—When heated with (*a*) 60% sulphuric acid at 160—170°, (*b*) 60% sulphuric acid at 140—150°, and (*c*) syrupy phosphoric acid at 170—180°, the preceding nitro-compound was charred in (*a*) and recovered unchanged in (*b*) and (*c*). The nitro-compound (15 g.) was hydrolysed by heating with concentrated hydrochloric acid (30 c.c.) for 10 hours in a sealed tube at 120—140°. The blackish product was extracted with boiling benzene, the residue dissolved in aniline (5 c.c.), and absolute alcohol (10 c.c.) added. 1-Nitrocarbazole (2 g.), m. p. 187—188°, then separated [Found : N, 13·4, 13·7 (W. and S.). Calc. : N, 13·2%]. Morgan and Mitchell (*loc. cit.*) give m. p. 186·5—187·5°.

1-*Benzamidocarbazole*, prepared from 1-aminocarbazole and benzoyl chloride in pyridine and crystallised from ethanol, had m. p. 242° (Found : N, 9·95. $C_{19}H_{14}ON_2$ requires N, 9·8%).

1-*Amino*-9-p-*toluenesulphonylcarbazole*.—1-Nitro-9-*p*-toluenesulphonylcarbazole (25 g.) was boiled with rectified spirit (400 c.c.), tin (25 g.) and concentrated hydrochloric acid (50·0 c.c.) added during 1 hour, and the mixture heated on a boiling water-bath for 11 hours. The alcohol was distilled off, and the residual solution basified with caustic soda; the precipitate was extracted with hot alcohol, which depositied, on cooling, 6·2 g. of the *amino*-compound. The alcoholic mother-liquor on addition of water gave an oily product, which after crystallisation as the hydrochloride gave another 12 g. of the amine. It formed crystals from ethanol, m. p. 134° [Found : N, 8·5, 8·2 (W. and S.). $C_{19}H_{16}O_2N_2S$ requires N, 8·3%].

The amino-compound was decomposed, not hydrolysed, by hydrochloric acid and by 50% sulphuric acid.

1-*Acetamido*-9-p-*toluenesulphonylcarbazole*, m. p. 8·8° (Found : N, 7·7. $C_{21}H_{18}O_3N_2S$ requires N, 7·4%), 1-*benzamido*-9-p-*toluenesulphonylcarbazole*, m. p. 165° (Found : N, 6·5. $C_{26}H_{20}O_3N_2S$ requires N, 6·4%), and 1-p-*toluenesulphonamido*-9-p-*toluenesulphonylcarbazole*, m. p. 241° (Found : N, 6·0; S, 12·95. $C_{26}H_{22}O_4N_2S_2$ requires N, 5·7; S, 13·1%), were prepared by the action of acetic anhydride, benzoyl chloride and pyridine, and *p*-toluenesulphonyl chloride and pyridine, respectively, and crystallised from ethanol.

3-*Bromo*-9-p-*toluenesulphonylcarbazole*.—A solution of 9-*p*-toluenesulphonylcarbazole (10 g.) in glacial acetic acid (60 c.c.) at 60° was stirred while bromine (5·2 g.) in acetic acid (10 c.c.) was added (1 hour); the mixture was then stirred at 70° for 2 hours. After cooling, the crystals were removed and the mother-liquor added to ice-water, giving more of the bromo-compound (total yield, 12 g.), m. p. 148° after crystallisation from ethanol (Found : Br, 20·0. $C_{19}H_{14}O_2NBrS$ requires Br, 20·0%). The same *substance*, m. p. and mixed m. p. 148° (Found : Br, 20·0%), was obtained by converting 3-bromocarbazole into its *p*-toluenesulphonyl derivative.

Dinitro-9-p-*toluenesulphonylcarbazole*.—A solution of the sulphonylcarbazole (10 g.) in glacial acetic acid (60 c.c.) at 70°, after addition of 98% nitric acid (5·0 g.) during 40 minutes, was kept at 70—80° for 3 hours, at 80—85° for 2 hours, cooled, and poured on ice. The nitro-compound (11 g.) was extracted with boiling toluene (200 c.c.). The residue and the crystals from the toluene solution were crystallised from nitrobenzene, giving 6·1 g., m. p. 207° (Found : N, 10·25; *M*, ebullioscopic in acetone, 405·8. $C_{19}H_{13}O_6N_3S$ requires N, 10·2%; *M*, 411), and 2·0 g., m. p. 271° (Found : N, 10·3%), very sparingly soluble in acetone. Neither compound could be hydrolysed by normal methods.

Nitration of 1-*Nitro*-9-p-*toluenesulphonylcarbazole*.—The carbazole (1 g.) was nitrated in glacial acetic acid (6 c.c.) at 80° (97% nitric acid, 0·45 g.) and after ½ hour the temperature was kept at 100° for 1 hour, and the mixture then poured into ice-water. The product (1 g.) was fractionally crystallised from amyl alcohol and acetone–ether, giving 0·4 g., m. p. 203°, and 0·2 g., m. p. 268°, identical with the two *dinitro*-compounds described above, and a product (0·2 g.) m. p. 120—130°, from the mother-liquors.

Nitration of 3-*Nitro*-9-p-*toluenesulphonylcarbazole*.—This *compound*, prepared from 3-nitrocarbazole by the usual acetone method, crystallised from amyl alcohol in fine needles, m. p. 211° (Found : N, 7·4. $C_{19}H_{14}O_4N_2S$ requires N, 7·65%). It (1 g.) was nitrated in glacial acetic acid (3 c.c.) and acetic anhydride (3 c.c.) at 30° (98% nitric acid, 1 c.c.) and after 1 hour the mixture was heated to 100° during 5 hours and poured into ice-water. The product (1·0 g.), crystallised from amyl alcohol and then from nitrobenzene, had m. p. 304° (Found : N, 10·3. $C_{19}H_{13}O_6N_3S$ requires N, 10·2%).

3 : 6-*Dinitro*-9-p-*toluenesulphonylcarbazole* was prepared from 3 : 6-dinitrocarbazole by the acetone method and crystallised from aniline and then from nitrobenzene; it had m. p. 302—303° and was apparently identical with the product obtained above.

The rates of nitration of 1- and 3-nitro-9-*p*-toluenesulphonylcarbazole were compared by mixing 1·0 g. of each substance with acetic acid (6 c.c.) and 98% nitric acid (0·5 c.c.) and stirring while the temperature was raised in 4 hours from 30° to 90°. The products were isolated, and the approximate extent of dinitration determined by (1) the titanous chloride method, (2) the percentage of nitrogen, (3) the molecular weight. The 1-nitro-compound gave roughly 60%, and the 3-nitro-compound only about 15%, of dinitro-product.

We thank the University of Rangoon for a grant in aid of this work, which it is hoped to continue. Analyses marked W. and S. were made by Drs. Weiler and Strauss of Oxford.

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95. *An Azeotrope of Nicotine and Water.*

By D. F. Kelly, (Miss) M. J. O'Connor, and J. Reilly.

Distillation constants have been applied to the examination of binary mixtures of liquids which form azeotropes. Mixtures of nicotine and water have thereby been proved to form an azeotrope, and this has been confirmed by investigation of the liquid–vapour equilibrium curve.

The authors showed (J., 1941, 275) that nicotine could be extracted from aqueous solutions by means of trichloroethylene, and fractional distillation of such solutions demonstrated the formation of an azeotrope of nicotine and water (*Nature*, 1941, **148**, 438). This has now been confirmed by determination of the distillation constants of aqueous solutions of nicotine and of the liquid–vapour equilibrium curve.

The distillation constants were determined by the method of Virtanen and Pulkki (*J. Amer. Chem. Soc.*, 1928, **50**, 3138). Reilly and Kelly (" Thorpe's Dictionary of Applied Chemistry," London, 1940, Vol. IV) have pointed out that the distillation constant, K, of a binary mixture determined by this method is the same as the relative volatility, α (Walker, Lewis, and McAdams, " Principles of Chemical Engineering," New York, 1937), of the constituents of the mixture. The similarity of K and α was considered to hold only on the condition that the constituents of a mixture obeyed Raoult's law. For a mixture composed of x_1 parts by weight of one liquid (*e.g.*, nicotine) and y_1 of another (*e.g.*, water) K is defined (following Virtanen and Pulkki, *loc. cit.*) by

$$K = (\log x_1 - \log x_2)/(\log y_1 - \log y_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which is derived from Brown's equation (J., 1881, **39**, 531) : x_2 and y_2 are the number of parts by weight of the respective constituents left in the mixture after a partial distillation.

To show the more general relationship of K and α the distillation of a binary mixture may now be viewed as follows. If A and B are the number of g.-mols. of the respective pure components (A and B) in a mixture being distilled, and if an infinitesimal amount of the mixture be boiled off (at its particular boiling temperature) then

$$-\mathrm{d}A/-\mathrm{d}B = p_A/p_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where p_A and p_B are the respective partial vapour pressures at that temperature. If α is the relative volatility of the components in the mixture, then by definition (Walker *et al.*, *op. cit.*)

$$\alpha = v_A/v_B = (p_A/m_A)/(p_B/m_B) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where v_A and v_B are the volatilities of the pure components (at the particular temperature of the boiling point) and m_A and m_B are the mol.-fractions of the respective components in the mixture. Substitution of the values $m_A = A/(A + B)$ and $m_B = B/(A + B)$ in (3) and rearrangement gives

$$p_A/p_B = \alpha A/B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and substitution of this value of p_A/p_B in (2) gives

$$-\mathrm{d}A/-\mathrm{d}B = \alpha A/B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If α is a constant for a finite partial distillation, then (5) gives on integration :

$$\ln(A_1/A_2) = \alpha \ln(B_1/B_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

or

$$(\log A_1 - \log A_2)/(\log B_1 - \log B_2) = \alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

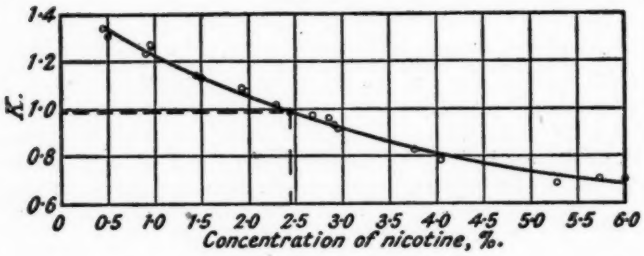
the subscripts 1 and 2 relating, respectively, to the composition of the " distilland " at the beginning and the end of the partial distillation. The same relationship (7) holds if composition is expressed by weight instead of by g.-mols. Equations (1) and (7) are therefore identical provided the relative volatility of the components be constant through the temperature range of the partial distillation. This condition is approximately observed in practice. Walker *et al.* (*op. cit.*) point out that, on change of temperature, although volatilities vary widely, yet relative volatilities, in general, vary but little. In practice, K will closely approximate to α; for an infinitesimally small distillation, the two would be identical. Azeotropic components deviate from Raoult's law, and with these, the identity will not hold in general : K will approximate to α if the deviations are small or if they nearly cancel. Experimental determination of K (or α) will indicate the existence of an azeotrope.

The experimental determination of true relative volatility, α, *e.g.*, by way of the liquid–vapour equilibrium points, is tedious, but Virtanen and Pulkki's method (*loc. cit.*) enables K to be determined easily and rapidly. Briefly, in this method, a mixture is distilled into separate small portions of distillate, leaving some residual " distilland," and the compositions of each are ascertained. The first portion of distillate being considered as arising from the combined remaining portions plus the residual " distilland," etc., values of K for a set of compositions equal to the number of portions of distillate are obtained. During any one partial distillation, it is assumed that the pertaining value of K of the components does not vary widely. The variation in K (or α approximately) over the whole range of compositions taken may be obtained quickly by finite partial distillation experiments even in the case of azeotropic components. In the latter case K will be determined for compositions which will fall to one side or other of the azeotropic composition.

The variation with composition of α is of interest in the case of binary mixtures forming azeotropes. If the components are present in the exact azeotropic composition, α is unity. At other compositions α is greater than or smaller than unity depending on which component is present in excess of this composition. When plotted, the curve of α–composition will go through the point $\alpha = 1$ at a point corresponding to the azeotropic composition. The same will hold true for K, which would remain constant at $K = 1$ throughout the distillation of an azeotropic mixture. Hence, determination of K for pairs of liquids by the rapid technique of Virtanen and Pulkki (*loc. cit.*) should afford, at least, a preliminary means of detecting the existence of an azeotrope. Distillation into separate portions of distillate could also be carried out by the more elaborate method of Rosanoff, Bacon, and White (*J. Amer. Chem. Soc.*, 1914, **36**, 1803), devised primarily for construction of liquid–vapour equilibrium curves. In that case, in addition to "extrapolating to zero" to obtain equilibria points, a series of values for K could be calculated for preliminary purposes.

For various nicotine–water mixtures K was determined by Virtanen and Pulkki's method. The results obtained are given in Table I. Curves of the first, second, and third degree were successively fitted to the data by using orthogonal polynomials and the method of least squares. Analysis of variance showed that the cubic did not materially improve the fit, and it was therefore not necessary to proceed beyond the second degree. The fitted quadratic was (q being the percentage of nicotine) $K = 1{\cdot}440427 - 0{\cdot}221455\,q + 0{\cdot}015837\,q^2$, and this curve, together with the data of Table I, are shown in Fig. 1. With this curve, $K = 1$ when $q = 2{\cdot}40$. The cubic curve gave $K = 1$ when $q = 2{\cdot}43$, which may be taken as the approximate composition of the azeotrope.

FIG. 1.



The experimental results tend to make K constant (*ca.* 0·7) for nicotine concentrations exceeding 5%, corresponding to the region where there are two liquid phases in the flask at the distillation temperature. In this region, the boiling point of the mixture is above the lower critical solution temperature of nicotine and water: the region represents compositions within the loop of the well-known closed solubility curve for nicotine–water solutions. It is noteworthy, too, that the distilland (at room temperature) and the distillates obtained in this region are one-phase liquid systems. When two liquid layers exist in the distilling flask (at the temperature of the boiling point of the mixtures) the distillation must be looked upon as follows: each layer, being a saturated solution, will maintain constant composition throughout the distillation, and the composition of the distillate (as well as the boiling point) will also be constant. Under these conditions, K must have a constant value as required by equation (1).

An aqueous solution containing 2·45% of nicotine distilled unchanged, K being approximately unity (actually 0·99) throughout the distillation, so this was taken to be the azeotropic composition. The azeotrope boiled at 99·6°/760 mm., and is a homoazeotrope of minimum boiling point (Swietoslawski, "Ebulliometry," New York, 1937) or a "pseudo-azeotrope" (Walker *et al.*, *op. cit.*). The latter term, however, does not imply that the present azeotrope does not behave like a true azeotrope: it is not clear whether the term is reserved only for a two-liquid-phase mixture which distils unchanged and thus corresponds to the binary heteroazeotrope of Swietoslawski (*op. cit.*).

There are but few experimental illustrations of liquid–vapour equilibria in partially miscible systems (see Glasstone, "Textbook of Physical Chemistry," London, 1940, p. 722): the present azeotrope may correspond to the apparently theoretical case II discussed by Glasstone (*loc. cit.*).

By Othmer's method (*Ind. Eng. Chem., Anal.*, 1932, **4**, 232) we determined the liquid–vapour equilibrium curve of nicotine and water directly, thus confirming the existence of the azeotrope. The curve obtained is given in Fig. 2; it intersects the diagonal at a composition corresponding to 2·45% of nicotine, *i.e.*, that of the azeotrope.

EXPERIMENTAL.

The materials used and the method of determining the nicotine concentrations were the same as those described in our previous paper (*loc. cit.*). For the distillation experiments, Virtanen and Pulkki's method and apparatus (*loc. cit.*) were employed. Solutions of nicotine and water were distilled (at a rate of *ca.* 1 c.c./min.), and the distillate collected in successive portions. The values of K obtained for different concentrations are given in Table I and plotted in Fig. 1, showing the approximate azeotropic composition. When 150 c.c. of a 2·45% solution of nicotine in water

TABLE I.

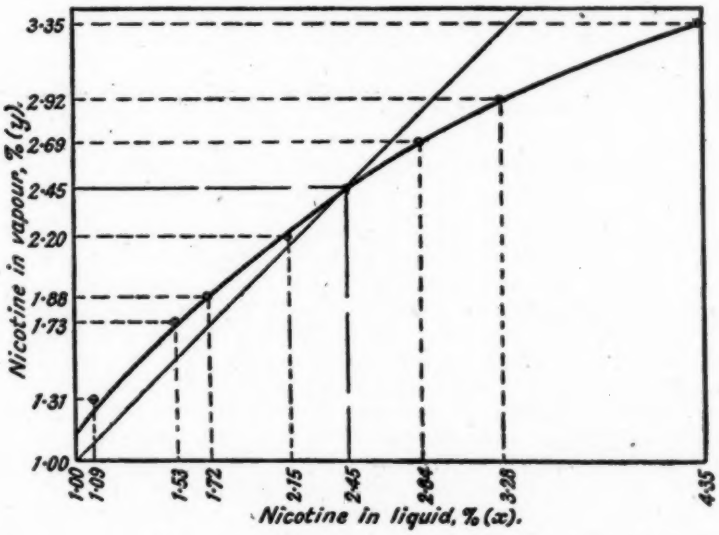
Nicotine, %	0·45	0·50	0·91	0·94	0·95	1·46	1·51	1·92	1·97	2·27	2·28
K	1·34	1·31	1·24	1·27	1·26	1·14	1·13	1·09	1·08	1·02	1·019
Nicotine, %	2·45	2·68	2·86	2·90	2·95	3·76	4·02	5·28	5·72	6·01	
K	0·99	0·97	0·96	0·93	0·92	0·82	0·78	0·69	0·7	0·7	

were distilled into 5 portions of distillate (*ca.* 25 c.c. each), no change in composition was found (apart from a negligible change in the last two) and a constant value of K was obtained (see Table II).

TABLE II.

Nicotine, %	2·45	2·45	2·45	2·46	2·46
K	0·99	0·99	0·99	0·99	0·99

FIG. 2.



The values given in Table III were obtained for equilibrium points in the liquid–vapour equilibrium curve (Fig. 2) as determined by Othmer's method (*loc. cit.*). An aqueous solution of nicotine was boiled in a still of the prescribed type until equilibrium was set up. Samples were drawn off from the still and distillate receiver, and their compositions

TABLE III.

Nicotine in liquid (x), %	1·09	1·53	1·72	2·15	2·84	3·28	4·35
Nicotine in vapour (y), %	1·31	1·73	1·88	2·20	2·69	2·92	3·35
α	—	1·11	1·10	1·02	0·92	0·89	0·76

ascertained as before. The figures obtained gave a pair of equilibrium compositions, and further pairs were determined similarly. Unduly prolonged boiling in the apparatus was avoided, for the solutions became brown.

The true relative volatilities, α, of nicotine and water are also given in Table III for the respective equilibrium compositions. These values of α are calculated from the expression $\alpha = (b/a)[(1 - a)/(1 - b)]$, where a and b are the equilibrium compositions (expressed as proportion of nicotine) of liquid and vapour respectively. The value of α for the first pair of compositions was not calculated as this pair of values did not lie on the smooth curve.

Dr. M. D. McCarthy is responsible for the mathematical part of this paper, and we wish to thank him for his assistance.

UNIVERSITY COLLEGE, CORK. [*Received, January 14th*, 1942.]

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96. *Rubber, Polyisoprenes, and Allied Compounds. Part II. The Molecule-linking Capacity of Free Radicals and its Bearing on the Mechanism of Vulcanisation and Photo-gelling Reactions.*

By ERNEST HAROLD FARMER and STEPHEN E. MICHAEL.

It is known that when dibenzoyl peroxide is heated with rubber at 140° interaction takes place and the rubber undergoes a species of vulcanisation. To elucidate the course of this reaction the behaviour of dibenzoyl peroxide towards a typical olefin, *cyclo*hexene, has been examined. Numerous products, including C_6- and C_{12}-hydrocarbons and benzoates of these, are formed, the reaction involving the thermal decomposition of the peroxide to give free phenyl and benzoate radicals. These radicals lead to (*a*) the interlinking of the olefin molecules, and (*b*) the formation of derivatives of both the simple and the " polymeric " olefins. The olefin molecules are attacked by the radicals principally at the α-methylene groups, but in part at the double bonds. The results described not only disclose an important reactivity of olefins but afford an explanation of numerous vulcanisation reactions which rubber undergoes, and also of certain photo-gelling reactions which are promoted by free-radical sources.

OSTROMISLENSKY (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1885) discovered that dibenzoyl peroxide when heated with rubber to 140° brought about a species of vulcanisation of the rubber, the chemical nature of which has

been the subject of much conjecture and experimental investigation. It was at first thought that the process was essentially one of oxidation, and indeed, free benzoic acid derived from the peroxide was isolated by Ostromislensky from the reaction product; but van Rossem, Dekker, and Prawirodipoero (*Kautschuk*, 1931, **7**, 202, 220) found that, although much benzoic acid was liberated during the reaction, some became united with the rubber, and could afterwards be freed by saponification. Van Rossem and his collaborators, however, were unable to correlate the accumulated observations with the previously published generalisations of Gelissen and Hermans (*Ber.*, 1926, **59**, *B*, 662) concerning the nature of the reactions between dibenzoyl peroxide on the one hand and numerous substances, including alcohols, organic acids, and saturated and benzenoid hydrocarbons, on the other; nevertheless, they agreed with Gelissen and Hermans on one point, *viz.*, that to some extent cleavage of the peroxide with formation of benzoic acid probably occurred, and they suggested that the concomitant reaction was a dehydrogenation of the rubber, the latter possibly becoming cross-linked as the result ($2\cdot C_5H_8 + Ph\cdot CO\cdot O\cdot O\cdot COPh \longrightarrow \cdot C_5H_7\cdot C_5H_7\cdot + 2Ph\cdot CO_2H$). Subsequently, Ostromislensky ("Rubber Chemistry and Technology," 1937, p. 279), following useful observations by Bock (*Kautschuk*, 1931, **7**, 224), made a new examination of the reaction and concluded that it proceeded according to the equation:

$$(C_5H_8)_n + n Ph\cdot CO\cdot O\cdot O\cdot COPh \longrightarrow n Ph\cdot CO_2H + (C_5H_7O\cdot COPh)_n$$

If this view is correct, the net result of the interaction must be the *substitution* of a benzoate group in each reacting isoprene unit of the rubber chain, presumably without materially decreasing the number of the original double bonds. Evidence that the reaction does indeed occur without substantial diminution in the original unsaturation had earlier been contributed by Fisher and Gray (*Ind. Eng. Chem.*, 1928, **20**, 294).

In view of recent developments relating to the formation of free radicals during the thermal decomposition of dry or dissolved dibenzoyl peroxide (cf. Hey and Waters, *Chem. Rev.*, 1937, **21**, 169), it appeared fairly certain that Ostromislensky's equation is an over-simplified representation of the phenomena involved. For further advance in the matter, however, it seemed desirable to examine in some detail the possibilities of reaction between dibenzoyl peroxide and some convenient simple olefin. That simple olefins readily react with dibenzoyl peroxide was effectively shown by Lippmann (*Monatsh.*, 1884, **5**, 562), who heated amylene with the peroxide at 100° and obtained definite (although doubtless incorrectly identified) products; * that the scope for the exercise of such reactivity is wide is already apparent from the ever-increasing list of condensations and "polymerisations" amongst olefinic substances which can be promoted by dibenzoyl peroxide or other peroxidic material. The simplest analogue of rubber is trimethylethylene, $H[CH_2\cdot CMe{:}CH\cdot CH_2]H$, but since in this hydrocarbon the α-methylene groups are somewhat modified in character by being incorporated in methyl groups, *cyclo*hexene was chosen for examination in its place.

When a *large excess* of *cyclo*hexene was heated with dibenzoyl peroxide to 140° in a closed vessel, all the peroxide disappeared, and most of its substance entered into combination with the *cyclo*hexene. Carbon dioxide was formed during the reaction, causing increase of pressure. The reaction product contained some benzoic acid but no significant proportion of any other acidic material. The neutral portion of the product consisted of a number of hydrocarbons of the C_6- and C_{12}-series, and various benzoates derived from these hydrocarbons.

If the free-radical basis of the thermal decomposition of dibenzoyl peroxide as advanced by Hey and Waters is accepted, the radicals to be expected from the decomposed peroxide are Ph^- and $Ph\cdot CO\cdot O^-$, and these may be expected to react with the very abundant *cyclo*hexene molecules, either (*a*) extracting hydrogen atoms from them and so forming *cyclo*hexenyl radicals and radical hydrides RH (where R = Ph or Ph·CO·O),

$$(a)\ C_6H_{10} + R^- \longrightarrow C_6H_9^- + RH \qquad (b)\ C_6H_{10} + R^- \longrightarrow C_6H_9R + H^-,$$

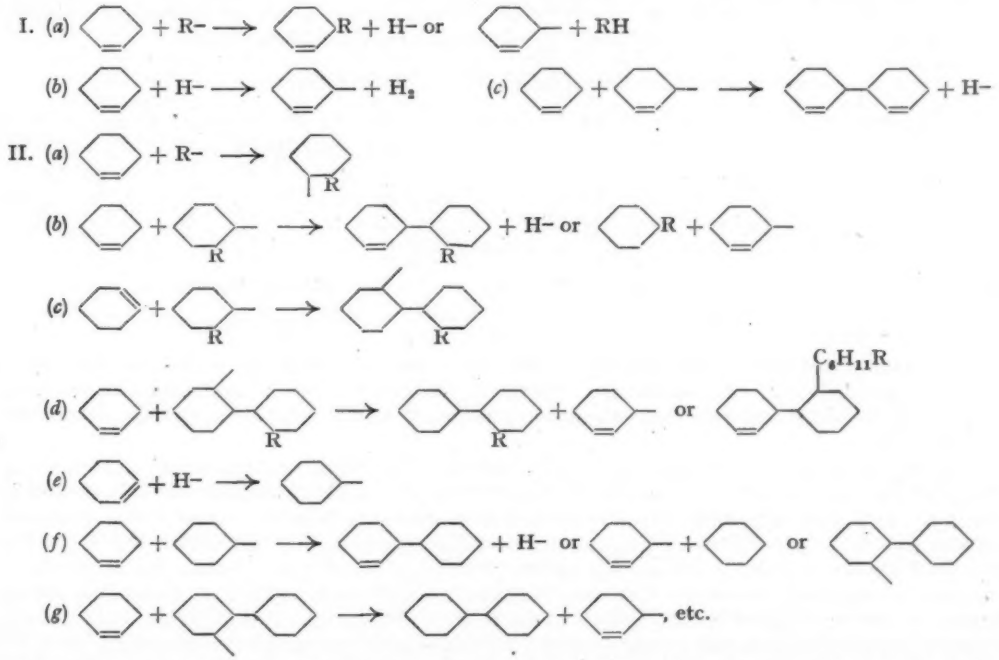
or (*b*) expelling hydrogen atoms from them and themselves coupling with the resulting residues. Any olefin, however, which contains the grouping $\cdot CH_2\cdot CH{:}CH\cdot$ has two outstanding characteristics: (1) the exceptional ease with which α-methylenic hydrogen atoms can be detached (cf. Farmer and Sundralingam, this vol., p. 121, and forthcoming publications), and (2) the usual high reactivity of the double bond. The first characteristic is likely to ensure that, in spite of the general capacity of a free radical to displace a hydrogen atom from any saturated carbon atom in the *cyclo*hexene ring, the actual displacement will occur at one of the α-methylene groups. The second characteristic is of somewhat uncertain importance in the present connexion, since there is no very clear evidence to show how far attack by free radicals at the double bond in the manner (*c*) is likely to succeed, although recent investigations indicate that bromine *atoms* by adding at one end of an

$$(c)\ \cdot CH{:}CH\cdot + R^- \longrightarrow {}^-CH\text{–}CHR$$

ethylenic bond can initiate the "abnormal" type of hydrogen bromide addition to olefins (Kharasch *et al.*, *J. Org. Chem.*, 1937, **2**, 288; *J. Amer. Chem. Soc.*, 1933, **55**, 2468, 2521, 2531), the *cis-trans*-rearrangement of stilbene (*idem*, *ibid.*, 1937, **59**, 1155; Taylor and Murray, J., 1938, 2078), and a species of oxygen addition to olefins (Bockemüller and Pfeuffer, *Annalen*, 1939, **537**, 178); also that sulphite radicals in a similar way can initiate the addition of sodium sulphite to olefins (Kharasch, *J. Org. Chem.*, 1938, **3**, 175), and likewise radical-molecules probably unite with olefin molecules and give by repetition of the process long macropolymeric chains (cf. Melville, J., 1941, 419).

* Gelissen and Hermans' interpretation of the course followed by Lippmann's reaction (*Ber.*, 1925, **58**, 2396) is in our view erroneous.

If reaction according to (*c*) does occur to an appreciable extent, the number of possible products from dibenzoyl peroxide and *cyclo*hexene will be considerably increased, and the main lines of reaction are then likely to include the following specific reactivities,* in which R^- represents a free radical derived by decomposition of dibenzoyl peroxide.



Since $R^- = Ph^-$ or $Ph{\cdot}CO{\cdot}O^-$, the products according to (I) should be : *benzene, benzoic acid,* Δ^2-cyclo*hexenyl benzoate,* 3-*phenyl*-Δ^1-cyclo*hexene,* and $\Delta^{2'}$-cyclo*hexenyl*-Δ^2-cyclo*hexene,* whilst those according to (II) should be : 2′-phenyl*cyclo*hexyl-Δ^2-*cyclo*hexene, 2-$\Delta^{2'}$-cyclo*hexenyl*cyclo*hexyl benzoate,* phenyl*cyclo*hexane, cyclo*hexyl benzoate,* 1-phenyl-2-*cyclo*hexyl*cyclo*hexane, 2-*cyclo*hexyl*cyclo*hexyl benzoate, Δ^2-*cyclo*hexenyl-[*cyclo*hexyl-2′]-[*cyclo*hexyl-2″] benzoate, Δ^2-*cyclo*hexenyl-[*cyclo*hexyl-2′]-[*cyclo*hexyl-2″]-benzene, 3-*cyclo*hexyl*cyclo*hexene, *cyclo*hexane, *cyclo*hexyl*cyclo*hexane, etc.

The reaction products actually isolated, or otherwise identified, are shown in italics in the above list, but in addition to these, *cyclo*hexane and *cyclo*hexyl*cyclo*hexane, which would be difficult to recognise in the mixture, may well have been present in appreciable amount; phenyl*cyclo*hexane also may have been present in minor amount. The presence of *cyclo*hexyl*cyclo*hexene is doubtful. Tricyclic reaction products were not well represented, but in the highest-boiling fractions obtained from the reaction mixture the principal component (*cyclo*hexenyl*cyclo*hexyl benzoate) appeared to be admixed with appreciable proportions of tricyclic hydrocarbons (see p. 519). The substances which were found to be present in largest proportion were benzoic acid, *cyclo*hexenyl benzoate, *cyclo*hexyl benzoate, *cyclo*hexenyl*cyclo*hexene, and *cyclo*hexenyl-*cyclo*hexyl benzoate, but benzene, the yield of which could not be reliably determined, was probably also a major product.

A number of conclusions are to be drawn from the character and quantitative proportions of the chief reaction products. (1) The main bulk of the free radicals formed by decomposition of the peroxide attack the olefin molecules at the α-carbon atoms, although some not inconsiderable degree of attack apparently succeeds at the double bond. (2) It is clear that somewhere about half the $Ph{\cdot}CO{\cdot}O{\cdot}$ groups present in the peroxide (2 per molecule) survive in the form of benzoates, but it is not clear whether all the peroxide molecules decompose in the fashion (A) or whether some can decompose in the fashion (B). (3) The interlinking of hydro-

(A) $Ph{\cdot}CO{\cdot}O{\cdot}O{\cdot}COPh \longrightarrow Ph{\cdot}CO{\cdot}O{\cdot} + CO_2 + Ph{\cdot}$
(B) $Ph{\cdot}CO{\cdot}O{\cdot}O{\cdot}COPh \longrightarrow 2Ph{\cdot}CO{\cdot}O{\cdot}$

carbon molecules, whether it occurs by the action of olefin or hydro-olefin free radicals on ordinary olefin molecules (*e.g.*, reactions I*c*, II*f*, II*g*), or of benzoate-substituted- or phenyl-substituted-hydro-olefin radicals on ordinary olefin molecules (*e.g.*, reactions II*b*, II*c*, II*d*), constitutes a very large proportion of the total reactivity observed. (4) Interlinking of olefin molecules is confined almost entirely to the " dimeric " stage of reaction, although a little phenyl-substituted " dimer " appears to have been formed. (5) *cyclo*Hexenyl-*cyclo*hexenyl benzoate, $C_6H_9{\cdot}C_6H_8{\cdot}O{\cdot}COPh$, occurs among the minor reaction products but does not appear in

* In view of the large excess of *cyclo*hexene used, any direct union of free radicals to give R_2 is likely to be very small in amount and is neglected.

the schemes I or II; hence it is necessary to conclude that *cyclo*hexenyl*cyclo*hexene, $C_6H_9 \cdot C_6H_9$, which is formed in considerable yield is subsequently attacked to some small extent by benzoate radicals.

In view of these results it is not surprising that the action of dibenzoyl peroxide on rubber consists largely in the attachment of numerous benzoate groups to the carbon chain (to a maximum of one benzoate group per unit) without material destruction of the original unsaturation of the rubber being caused. These groups doubtless become substitutionally attached at one or other of the α-carbon atoms of the isoprene units, but probably mainly at the α-methylene groups adjoining the methylated carbon atoms, thus :

$$\cdot CH(OBz) \cdot CMe{:}CH \cdot CH_2 \cdot CH(OBz) \cdot CMe{:}CH \cdot CH_2 \cdot$$

This substitution, however, will be only one of the *two* main results of the reaction with benzoyl peroxide, the second of which will involve the linking together of the rubber chains—probably largely at the α-methylene groups (most usually the α-methylene groups adjoining the methylated carbon atoms) as in (*h*), but probably to some extent also at an ethylenic carbon atom in one of the interlinking units as in (*j*) or (*k*), and possibly to some minor degree in one of the other ways typified in the reactions II, (*a*)—(*g*). Some small degree of phenyl substitution in the unlinked chains according to reaction I(*a*) is also likely to have occurred.

$$\begin{array}{l} \cdot CH \cdot CMe{:}CH \cdot CH_2 \cdot \\ \quad\vert \\ \cdot CH \cdot CMe{:}CH \cdot CH_2 \cdot \end{array} \quad (h) \qquad \begin{array}{l} \cdot CH \cdot CMe{:}CH \cdot CH_2 \cdot \\ \quad\diagdown \\ \cdot CH_2 \cdot CMe \cdot CH(OBz) \cdot CH_2 \cdot \end{array} \quad (j) \qquad \begin{array}{l} \cdot CH \cdot CMe{:}CH \cdot CH_2 \cdot \\ \quad\diagdown \\ \cdot CH_2 \cdot CH \cdot CMe(OBz) \cdot CH_2 \cdot \end{array} \quad (k)$$

As regards the widespread use of dibenzoyl peroxide and other peroxides for promoting the chemical aggregation, " polymerisation " or " condensation " of many different types of molecules, there is every reason to believe that free radicals from the decomposing peroxide initiate the cross linking, which can be continued by chain reactions.

It might be anticipated that other compounds which break down either spontaneously or on heating to give free radicals would have an action on olefins (and particularly on rubber) precisely analogous to that of dibenzoyl peroxide. It is not surprising therefore to find that diazo-compounds, whose strong tendency to break down to give free radicals and gaseous nitrogen is now well recognised (Hey and Waters, *loc. cit.*; Waters *et al.*, J., 1937, 2007 *et seq.*), are active vulcanising agents (Buizov, *J. Russ. Phys. Chem. Soc.*, 1921, **53**, 166) for rubber. Buizov worked with diazoaminobenzene, but later Levi (*Gomma*, 1937, **1**, 4) found that all diazoamino-compounds of the constitution R·N:N·NXR′, where R is an aryl group, R′ is an aryl-, aralkyl- or arylamino-group, and X is hydrogen, a metal, an alkyl-, acyl-, aryl- or aralkyl-group, are vulcanising agents. Also Levi observed that diazo-compounds which were effective vulcanising agents evolved nitrogen when they were heated to the usual vulcanisation temperature (*ca.* 140°),* and oxidation played no part in the vulcanising reaction. The reality of the active participation of free radicals is to be deduced from Levi's observation that diazoaminobenzene when heated alone at 150° gave 1 mol. of nitrogen and both *o*- and *p*-aminodiphenyl, a decomposition which may be represented :

$$NPh{:}N \cdot NHPh \longrightarrow Ph^- + NHPh^-$$
$$Ph^- + NHPh^- \longrightarrow Ph \cdot C_6H_4 \cdot NH^- + H^- \longrightarrow Ph \cdot C_6H_4 \cdot NH_2$$

Furthermore, Fisher (*Ind. Eng. Chem.*, 1939, **31**, 1381) has found, not only that 2 : 4 : 6 : 2′ : 4′ : 6′-hexachlorodiazoaminobenzene readily vulcanises rubber, but that some of the reagent (which presumably means fragments of the reagent molecules) adds to the rubber giving some hexachlorodiphenylamine as a by-product.

The symmetrically substituted diphenyl- and tetraphenyl-hydrazines are known to decompose readily into free radicals and these are found to produce a " stiffening " effect on rubber when kneaded into it. On the contrary, monosubstituted alkyl- and aryl-hydrazines, as well as *as*-diphenylhydrazines, act as softeners of rubber (Williams and Smith, *Ind. Eng. Chem.*, 1935, **27**, 1317), from which it may be deduced that they are promoters of oxidation, presumably functioning for this purpose in a similar manner to pyridine (cf. Farmer and Sundralingam, this vol., p. 128).

Perhaps, however, the most interesting example of an effective vulcanising agent is tetramethylthiuram disulphide, $CHMe_2 \cdot CS \cdot S \cdot S \cdot CS \cdot CHMe_2$, which is a close sulphur analogue of dibenzoyl peroxide. The capacity of this substance to yield free radicals spontaneously or on heating has, so far as we are aware, not been demonstrated, but it is remarkable that this disulphide is not only by itself an excellent vulcanising agent for rubber, but is a first-rate accelerator of sulphur vulcanisation. The method of action of accelerators has never been determined, but it seems not unlikely that the effectiveness of at least some of them is due to their capacity to yield free radicals spontaneously or on heating, either when used in the form of their zinc salts (*e.g.*, dithiocarbamates, $R_2N \cdot CS \cdot SH$; thiolbenzthiazole, $C_6H_4\langle^{N}_{S}\rangle C \cdot SH$) or when used directly [*e.g.*, tetramethylthiuram disulphide; di(benzthiazolyl) disulphide, $C_6H_4\langle^{N}_{S}\rangle C \cdot S \cdot S \cdot C\langle^{N}_{S}\rangle C_6H_4$].

Ostromislensky's reaction between dibenzoyl peroxide and rubber appears to involve two distinct features, *viz.*, the interlinking of rubber units (which process may be inter- or intra-molecular and so take the form of cross linking of molecules or cyclisation reactions), and the addition of fragments to the rubber chain. This

* Curiously enough, diazonium chlorides, $R \cdot N_2Cl$, in spite of their decomposability at vulcanisation temperatures, were found not to serve as vulcanising agents.

dual type of reaction probably extends also to sulphur vulcanisations, and to vulcanisations in which the action of sulphur is assisted by an organic accelerator. The exact course of reaction in either of these cases is uncertain, but in both cases the production of a satisfactory vulcanised structure as determined by a physical test (the tensile strength *) is but little dependent on the loss of original unsaturation in the rubber. Thus Brown and Hauser (*ibid.*, 1938, **30**, 1291; 1939, **31**, 1225) have found that the optimum (physical) state of vulcanisation of rubber obtained when tetramethylthiuram disulphide is the vulcanising agent (*i.e.*, when no free sulphur is used) occurs when $<2\%$ of the original rubber-unsaturation has been lost, and an average of 0·25 atom of sulphur per C_5H_8 unit has been incorporated in the rubber chain. At this point chemical incorporation of sulphur in the rubber stops, and if heating at the vulcanisation temperature (141°) is continued, it causes little further diminution in the unsaturation. When the vulcanising agent is sulphur, used in conjunction with a small proportion of active accelerator, the loss of unsaturation on vulcanisation appears in most examples to amount only to several units % at the point of optimum vulcanisation; but often chemical incorporation of sulphur continues beyond this point, and concurrently the unsaturation usually continues to decrease, although the amount of this decrease varies considerably from accelerator to accelerator. For sulphur used alone as vulcanising agent a larger decrease in unsaturation than the foregoing value was observed at the point of optimum vulcanisation, and both the incorporation of sulphur and the decrease in unsaturation continued rapidly beyond this point. The best vulcanisates over the range of experiments were obtained when the proportion of combined sulphur at the point of optimum vulcanisation amounted to *ca.* 2 atoms per double bond lost, and not to 1 atom as has previously been supposed. It appears, therefore, from these observations that the incorporation of sulphur, and the concurrent saturation of double bonds can continue (especially if sulphur alone is used) after the essential work of vulcanisation is completed, and this reactivity may perhaps be considered as a side reaction which, although having an effect on the properties of the vulcanisates, is subsidiary to the basic process of vulcanisation.

Such subsidiary saturation of the double bonds could conceivably be caused by the direct addition of hydrogen sulphide, if sufficient of this reagent were generated in the vulcanisation reaction (for which there is little direct evidence), or alternatively it might result from a secondary reaction following after the primary reaction at the α-methylene carbon atoms; on the other hand, it is quite unlikely, in view of the usual incapacity of sulphur to act as an addendum for olefins, to be caused by the direct addition of sulphur at the double bonds. The fact that sulphur reacts readily with unconjugated di- and poly-olefinic substances such as linoleic and linolenic esters and glycerides (these substances showing a marked tendency for the ordinary olefinic additivity to be replaced by an α-methylenic substitutive tendency) suggests that the initial attack by sulphur in the sulphur-vulcanisation reaction may occur (like that of oxygen) at the α-methylene groups, and may possibly be succeeded (somewhat comparably with secondary autoxidation processes) by one or several types of secondary reaction which cause saturation of the double bonds. Such α-methylenic attack by sulphur may well be initiated by extraneous free radicals formed under vulcanisation conditions, or possibly by free radicals formed by direct thermal dissociation of α-methylenic hydrogen atoms. The precise course of reaction, however, remains to be determined.

Another phenomenon which appears to involve the production of a vulcanised structure in which the incorporation of foreign atoms or fragments in the hydrocarbon chains plays a part is the photo-gelling of dissolved rubber. The absolute dependence of this phenomenon on sunlight or ultra-violet light, its entire independence of any concurrent autoxidation process,† and also its promotion by acetone, acetophenone, benzophenone, etc., and by certain halogenated solvents (carbon tetrachloride, ethylene dibromide, chloroform, chloro- and dichloro-benzene, dichloro- and trichloro-ethylene, in order of decreasing efficiency) which not only are themselves prone to undergo photochemical decomposition with formation of free radicals, but can contribute these radicals (alkyl groups formed from the ketones, and chlorine atoms and chlorinated fragments from the halogenated solvents) to the interlinking hydrocarbon units or molecules, all suggest that the gelling takes a course closely analogous to those represented above for *cyclo*hexene and dibenzoyl peroxide. Stevens (*Trans. Inst. Rubber Ind.*, 1940, **16**, 211) has described the progress of gelling with the above-mentioned and other promoters, one or more of these usually acting as solvents for the rubber. Mixtures of acetone and carbon tetrachloride are particularly effective as promoters, and ethyl ether containing peroxides or acting in the presence of such peroxides as barium peroxide is also successful. Benzoyl peroxide in carbon tetrachloride–acetone acts very slowly in the dark, but more effectively under illumination to give extensively chlorinated gels, thus suggesting that, although in general free-radical decomposition of peroxides promoted by light can initiate the gelling reaction, yet a slow thermal decomposition similar to that which occurs in Ostromislensky's reaction at 140° can also feebly initiate gelling in conjunction with carbon tetrachloride–acetone. The gels produced differ in consistency, according to the efficiency of the promoters used, from tenuous gels, which oxidise readily in the presence of air and light to regenerate liquids, to tough materials easily cut by scissors. The dried rubbers recovered from the gels by evaporation of the solvent differ correspondingly in physical properties, but the extent to which the gelling promoters have become incorporated is shown by the large increases in weight, and in the case of halogenated promoters by the substantial halogen contents, most of which remain after treatment of the materials by boiling alcoholic potash. As would be expected, the physical

* This is only one, although a very important one, of the usual criteria of satisfactory vulcanisation.
† Oxygen, if present, delays gelling.

properties of the dried halogenated photo-gels obtained from rubber by means of dibenzoyl peroxide dissolved in carbon tetrachloride–acetone differ considerably from those of rubber vulcanised by Ostromislensky's procedure.

The profound difference between the result of irradiating rubber in presence of a potential source of free radicals such as acetaldehyde, first in strict absence of oxygen, and then in presence of oxygen, is clear from experiments of Spence and Ferry (*J. Soc. Chem. Ind.*, 1939, **58**, 345; *J. Amer. Chem. Soc.*, 1937, **59**, 1468). Under the first conditions vulcanisation or " polymerisation " occurs in the manner described above, and in the second, rapid autoxidation of the rubber sets in with oxidative scission of the hydrocarbon chains and " depolymerisation " of the rubber. The acetaldehyde in the latter conditions acts as a powerful autoxidation catalyst (see this vol., p. 144; Bloomfield and Farmer, *J. Soc. Chem. Ind.*, 1934, **53**, 121T).

Experimental.

Action of Benzoyl Peroxide on cyclo*Hexene*.—The peroxide (50 g.; 1 mol.) and *cyclo*hexene (200 c.c.; 9·6 mols.) were heated together in a stainless-steel autoclave or in sealed glass tubes at 140° for 6 hours. Carbon dioxide was produced and caused a small increase above atmospheric pressure in the cooled vessel. The resulting clear, slightly yellow liquid was shaken several times with 2N-sodium hydroxide, then with water, and finally it was dried over anhydrous sodium sulphate. The combined alkaline and aqueous washings were acidified, and the precipitated acid filtered off; it proved to be benzoic acid, m. p. 121° (equiv., 122), uncontaminated by any other acid.

The main reaction product was fractionally distilled: at atmospheric pressure, a forerun (I) (102 g.), consisting mainly of unchanged *cyclo*hexene, passed over, leaving a liquid residue which was divided into the following fractions by distillation at 0·1 mm. pressure: (II) (*a*) b. p. 70—74° (7·2 g.), (*b*) 74—110° (1·0 g.); (III) (*a*) 112—116° (33 g.), (*b*) 116° (2·0 g.), (*c*) residue in still (16·8 g.). The distillates were colourless liquids, the earlier ones mobile, the later ones viscous liquids. The residue was divided by distillation from a molecular (batch) still into the fractions: (IV) (*a*) bath-temperature 146—148° (12·9 g.), (*b*) bath-temp. 150—180° (1·1 g.), (*c*) yellow, very viscous, oily residue (2·8 g.), probably somewhat decomposed. This procedure was carried out numerous times with new batches of the reactants, but in the later experiments the re-fractionation of fraction (IV) was omitted.

Fraction (I). The forerun, although consisting mainly of *cyclo*hexene, was not homogeneous. The likely adulterants were *cyclo*hexane and benzene, but these were present in too small proportion to permit of their separation by careful fractional distillation, either directly, or after conversion of the *cyclo*hexene component into its dibromide; indeed, no satisfactory method of demonstrating the presence of a little *cyclo*hexane in the forerun was discovered. Spectroscopic examination, however, of the forerun showed unmistakably that a benzenoid compound was present. The absorption curves for (*a*) benzene in *cyclo*hexane, and (*b*) *cyclo*hexene in *cyclo*hexane at dilutions of 2½% and below show sufficiently marked differences to permit the presence of benzene to be distinguished at concentrations greater than 0·1%, and the presence of *cyclo*hexene at concentrations above 2%. When both benzene and *cyclo*hexene are present in *cyclo*hexane the former cannot be detected with certainty if the concentration of *cyclo*hexene is above *ca.* 3%, and the latter cannot be detected if the concentration of the benzene exceeds 0·1%; consequently, unless the concentration of benzene in the mixture is less than 1/30 of that of the *cyclo*hexene and itself exceeds 0·05%, its characteristic absorption will be masked by that due to the *cyclo*hexene. The absorption curves for (i) dilute solutions of benzene and *cyclo*hexene (together) in *cyclo*hexane, and (ii) dilute solutions of the forerun in *cyclo*hexane were found to be closely similar, but when solutions in *cyclo*hexane of the hydrogenated forerun (*i.e.*, forerun which had been hydrogenated as fully as possible at room temperature in presence of Adams's catalyst in order to convert *cyclo*hexene into *cyclo*hexane) were examined, the presence of benzene became unmistakable, and its concentration in the forerun was estimated to be 2·5%.

Fraction (II)(*a*). This fraction was an impure hydrocarbon of the C_{12}-series containing about 1% of oxygen and $n_{D}^{17\cdot4}$ (Found: C, 88·05, 87·9, 88·15; H, 10·95, 11·05, 10·95; iod. val., 272. Calc. for $C_{12}H_{18}$: C, 88·8; H, 11·2%; iod. val., 313).

A portion of this fraction (1 g.) was heated with powdered selenium (2 g.) at about 300° for 100 hours. The product was extracted with ether, the ether distilled, and the oily residue heated for a time over sodium. The liquid residue was freed from a little solid inorganic matter by dissolving it in ether, filtering, and removing the solvent; afterwards it was distilled. The bulk (0·5 g.) distilled at 98—108°/12 mm., and appeared to be unchanged hydrocarbon, but the succeeding portion distilled when the bath reached 200°, and solidified in the receiver. This solid was diphenyl, m. p. 69° (mixed m. p. 68—69°) (Found: C, 93·1; H, 6·75. Calc. for $C_{12}H_{10}$: C, 93·5; H, 6·5%).

Hydrogenation of a portion (4·7 g.) of this fraction in 5 c.c. of alcohol at room temperature and pressure in presence of Raney nickel (1240 c.c. of hydrogen absorbed, corresponding to 95·4% of that required for $C_{12}H_{18}$) gave a colourless liquid hydrocarbon, quite saturated to alkaline permanganate, but having too high a C/H ratio for *cyclo*hexyl*cyclo*hexane (Found: C, 87·3, 87·15; H, 12·75, 12·75. Calc. for $C_{12}H_{22}$: C, 86·65; H, 13·35%). Spectroscopic examination of the hydrogenated hydrocarbon side by side with pure *cyclo*hexyl*cyclo*hexane revealed U.V. absorption for the former approximately 100 times as strong as was shown by the latter, and an absorption band for the former in the appropriate region for benzene derivatives (2400—2550 A.; $\log_{m}\xi = 2{\cdot}0$); no individual maxima could, however, be observed. The curve for the hydrogenated hydrocarbon was approximately a mean between those of *cyclo*hexyl*cyclo*hexane and diphenyl, but it has not been possible to make direct comparison with the curve for pure phenyl*cyclo*hexane. The succeeding experiments confirm that the bulk of fraction (II)(*a*) was *cyclo*hexenyl*cyclo*hexene; the contaminant was doubtless mainly phenyl*cyclo*hexene, with possibly a little phenyl*cyclo*hexane.

A further portion of fraction (II)(*a*) (9 g.) was dissolved in chloroform and treated gradually at 0° with excess of N/5-bromine in chloroform (2 mols. of Br_2 per mol. of $C_{12}H_{18}$). The excess of bromine and most of the chloroform were evaporated at reduced pressure, whereupon much crystalline bromide separated (65% yield). This formed colourless prisms, m. p. 159°, from chloroform and proved to be $\Delta^{2'}$-cyclo*hexenyl*-Δ^{2}-cyclo*hexene tetrabromide* (Found: C, 29·8, 29·9; H, 3·9, 4·05; Br, 66·25. $C_{12}H_{18}Br_4$ requires C, 29·9; H, 3·75; Br, 66·35%). The tetrabromide appears to be identical with that, m. p. 158°, obtained by Cogan and Marvel (*J. Amer. Chem. Soc.*, 1934, **56**, 1815) from a hydrocarbon which they thought was probably di-Δ^{2}-*cyclo*hexenyl.

A portion of the tetrabromide (9 g.) was debrominated by zinc dust in alcoholic solution, giving thereby the parent hydrocarbon $\Delta^{2'}$-*cyclo*hexenyl-Δ^{2}-*cyclo*hexene, but this was contaminated with a little bromide (Found: C, 86·3; H, 10·6%). The constitution of the hydrocarbon was established by ozonisation of a portion in chloroform, without further purification, the ozonide giving on decomposition with water, and further oxidation of the product with dilute alkaline permanganate at 0°, a tetracarboxylic acid, $C_8H_{14}(CO_2H)_4$, which separated from ether (in which it was sparingly soluble) as a white crystalline powder, m. p. 177°. This was n-*octane-αδεθ-tetracarboxylic* acid (Found: C, 49·8; H, 6·45; equiv., 72·3. $C_{12}H_{18}O_8$ requires C, 49·65; H, 6·25%; equiv., 72·5).

The bromide recovered from the mother-liquors was freed as far as possible from the crystalline bromide, by crystallisation of the latter from light petroleum, and the solvent then completely removed at reduced pressure. The residual bromide was a brown viscous liquid (Found: Br, 59·3%). In order to remove from this any unbrominated (non-olefinic) hydrocarbons of the C_{12}-series, the liquid bromide was partly distilled, at 0·05 mm. pressure, whereupon only a few drops (0·1 g.) of impure hydrocarbon (Found: C, 81·05; H, 9·05%) passed over, leaving a residue which from its bromine content appeared to consist largely of a dibromide. This was probably, in view of the foregoing spectroscopic evidence, derived from phenyl*cyclo*hexene; some proportion of the dibromide of *cyclo*hexyl*cyclo*hexene, may, however, have been present.

Fraction (II)(*b*). This consisted of a mixture of C_{12}-hydrocarbon and the material of fraction (III).

Fraction (III)(*a*). This colourless oil of strong odour consisted of a mixture of benzoates of C_6-alcohols. The analytical values, which differed little from preparation to preparation, taken in conjunction with the iodine and benzoyl values, show that the mixture consisted of *cyclo*hexenyl benzoate and *cyclo*hexyl benzoate in roughly the proportion of 3 : 10 (Found: C, 76·55; H, 7·65; Bz, 59·4; iod. val., 38·4. Calc. for $C_6H_5{\cdot}CO_2C_6H_9$: C, 77·3; H, 6·9; Bz, 60·0%; iod. val., 125. Calc. for $C_6H_5{\cdot}CO_2C_6H_{11}$: C, 76·5; H, 7·85; Bz, 59·4%; iod. val., 0). The benzoyl value was determined by refluxing portions (6 g.) of the mixed esters with N-methyl-alcoholic sodium hydroxide (100 c.c.) in a nitrogen atmosphere for 5 hours, and then titrating with N-hydrochloric acid.

The mixed alcohols from the hydrolysed ester fraction were obtained by distilling off, through a column, the methyl alcohol from the basified hydrolysis products, and then thoroughly extracting the residue with ether. The ethereal solution after being dried (anhydrous sodium sulphate), gave a colourless, viscous liquid of strong smell. This was a mixture (*ca.* 1 : 4) of *cyclo*hexen-3-ol and *cyclo*hexanol (Found: C, 72·35; H, 11·65; iod. val., 64. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·3%; iod. val., 258·8. Calc. for $C_6H_{12}O$: C, 71·9; H, 12·1%). A crude α-naphthylurethane prepared from the mixture gave after several crystallisations from ether the pure α-naphthylurethane of *cyclo*hexanol, forming colourless needles, m. p. 128° (mixed m. p. 128°) (Found: C, 76·0; H, 6·8; N, 5·4. Calc. for $C_{17}H_{19}O_2N$: C, 75·8; H, 7·1; N, 5·2%); the corresponding derivative of *cyclo*hexen-3-ol was not isolated in pure form. Acidification of the alkaline hydrolysis liquor gave at once benzoic acid, which melted after one recrystallisation from water at 121°; no other aromatic acid could be found.

On addition of N/5-bromine in chloroform to a solution of the mixed alcohols (0·8 g.) in chloroform at 0°, 0·3 mol. of bromine was decolorised, and the product gave on removal of the solvent at reduced pressure a liquid from which by distillation (*a*) 0·5 g. of crystallisable *cyclo*hexanol, b. p. 60—64°/12 mm., and (*b*) 0·5 g. of 1 : 2-dibromo*cyclo*hexan-3-ol (clusters of needles, m. p. 55°, from light petroleum; mixed m. p. with authentic specimen of m. p. 55°, 55°. Found: C, 27·8; H, 4·2; Br, 62·4. Calc. for $C_6H_{10}OBr_2$: C, 27·9; H, 3·9; Br, 62·0%) were isolated.

Fraction (IV). The sub-fractions (*a*)—(*e*) were entirely saponifiable. Each fraction was analysed and then hydrolysed by 5 hours' heating with N-methyl-alcoholic sodium hydroxide. The derived alcohols were also analysed. It was apparent that no satisfactory fractionation had been achieved. A much better result was obtained by hydrolysing batches of fraction (IV) directly (*i.e.*, without any distillation) and isolating and fractionally distilling the derived alcoholic material at *ca.* 0·3 mm. pressure. Numerous such fractions were obtained having somewhat different composition and unsaturation, but the bulk of the material fell into three rather well-defined fractions: (i) a small amount of mobile liquid, b. p. 80°/0·3 mm., (ii) a viscous liquid, b. p. 90—100°/0·5 mm., (iii) a very viscous liquid, b. p. 100—118°/0·1 mm. The sub-fraction (i) resembled in all characteristics the mixture of *cyclo*hexanol and *cyclo*hexenol obtained by hydrolysis of fraction (III), and was not further examined. The sub-fraction (ii) was a mono-olefinic dicyclic alcohol, $C_{12}H_{20}O$ [Found: C, 80·2; H, 11·15; iod. val., 112; * *M* (in benzene), 185. Calc. for $C_{12}H_{20}O$: C, 79·9; H, 11·1%; iod. val., 141; *M*, 180]. This probably consisted mainly of Δ^2-*cyclo*hexenyl*cyclo*hexan-2-ol, although some proportion of its isomeride, 1-*cyclo*hexyl-Δ^2-*cyclo*hexen-4-ol, may have been present. The sub-fraction (iii), which distilled only with difficulty at 0·1 mm., gave carbon and molecular-weight values well above those required for a dicyclic alcohol of the C_{12}-series. The composition varied somewhat from preparation to preparation [*e.g.*, Found: (*a*) C, 83·5; H, 11·6; *M*, 206. (*b*) C, 84·0; H, 10·7; *M*, 214. (*c*) C, 82·8; H, 10·8%], but the range of variation in the hydrogen values was comparatively small. The fraction appeared to consist of a mixture of the dicyclic alcohols appearing in fraction (ii) with a minor proportion of a tricyclic hydrocarbon such as phenyl*cyclo*hexyl*cyclo*hexane (Calc.: C, 89·2; H, 10·8%; *M*, 242·2) or phenyl*cyclo*hexyl*cyclo*hexene (Calc.: C, 89·9; H, 10·1%; *M*, 240·2).

The acid obtained by saponification of fraction (IV) was homogeneous benzoic acid.

Yields.—The following table shows approximately the recovery of Ph·CO·O· groups (contained originally in the dibenzoyl peroxide) in a typical run employing 100 g. of peroxide and 400 c.c. of *cyclo*hexene.

Fraction.	Wt. (g.).	Wt. of Ph·CO·O· (g.).
(I) Forerun	—	—
(II) C_{12}-hydrocarbon	24	(*ca.*) 2
(III) Benzoates of C_6-alcohol	51	30—32
(IV) Benzoates of C_{12}-alcohol	31	12—13
Free benzoic acid	15	12—15
		Total 54—62

This shows that between 38% and 46% by weight of the original Ph·CO·O· groups in the peroxide had broken down during reaction and must thus have given rise to phenyl radicals and carbon dioxide amounting to 12—14% and 7—8% respectively of the weight of the original peroxide.

The above work has been carried out as part of the programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association. We thank Dr. W. T. Chambers for carrying out the analyses and Dr. G. A. Jeffrey for the spectroscopic examination of the hydrocarbon specimens.

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* The iodine values of all the sub-fractions derived by hydrolysis of Fraction (IV) were somewhat low. The corresponding hydrogen values were considerably lower still.

97. *Synthesis of Methyl α-Methoxyacrylate and α-Methoxyacrylonitrile: Characterisation of Methoxy-derivatives of Propionic Acid.*

By JOHN W. BAKER.

Satisfactory methods for the preparation of monomeric *α-methoxyacrylonitrile* and methyl α-methoxyacrylate have been worked out and, in the course of the investigation, a number of isomeric derivatives of methoxypropionic acids have been synthesised, characterised as their crystalline amides, and their constitutions established.

IN the course of investigations which had as their aim the synthesis of derivatives of α-alkoxyacrylic acids, various dimethoxy-, methoxyhydroxy-, and methoxyhalogeno-propionic esters have been prepared and their orientations established. All these esters are readily converted, by the action of cold aqueous ammonia, into highly crystalline amides, which are thus very convenient derivatives for the purpose of characterisation.

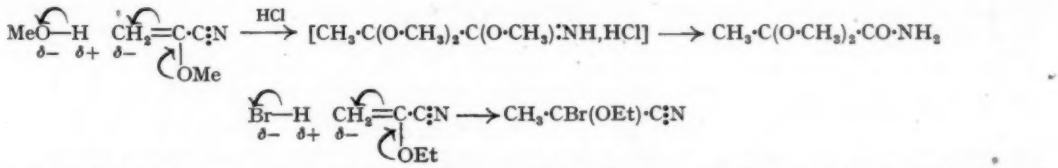
The initial line of attack was the action of sodium methoxide on halogenopropionic esters and this revealed points of interest regarding the relative reactivity of halogen substituents in the α- and the β-position. The main product of the action of two molecular proportions of methyl-alcoholic sodium methoxide on methyl αβ-dichloropropionate is a liquid of relatively high boiling point which contains chlorine. Its structure has not yet been established, but it is certainly formed by the interaction of more than one molecule of the halogeno-ester. When only one molecular proportion of sodium methoxide is used, the overall result is the replacement of the β-chlorine atom to give *methyl α-chloro-β-methoxypropionate*, characterised as its *amide* (I), m. p. 61°. The same ester (identified as the amide) is obtained when one molecule of sodium methoxide acts upon methyl α-chloro-β-hydroxypropionate. If this ester is formed by a direct bimolecular replacement, the greater reactivity of the primary halide (β-) than of the secondary (α-) is in harmony with the general conclusions from the recent work of Hughes, Ingold, and their collaborators (cf. *inter alia*, Hughes, *Trans. Faraday Soc.*, 1941, 603). Treatment of αβ-dibromopropionic acid with two molecular proportions of sodium methoxide in dry alcohol, however, gives a highly unsaturated sodium salt (probably sodium α-bromoacrylate) which, with a third molecule of sodium methoxide in the presence of a little quinol and subsequent acidification, affords a highly unsaturated acid, almost halogen-free. Esterification of this with dry methyl-alcoholic silver oxide and methyl iodide gives mainly *methyl αβ-dimethoxypropionate* (II), contaminated with a little unsaturated ester, since it is converted by ammonia into αβ-*dimethoxypropionamide* * (III), m. p. 58°, identical with a specimen prepared by methylation of methyl β-hydroxy-α-methoxypropionate (below) and conversion of the product into the amide. The formation of the same chlorine-containing amide from both the αβ-dichloro- and the α-chloro-β-hydroxy-ester proves that (I) is the α-chloro-β-methoxy-derivative. Confirmation of this structure is derived from the observation that (I) is isomeric, but not identical, with β-*chloro-α-methoxypropionamide* (IV), m. p. 138°, which was synthesised in the following manner. Methyl methoxyacetate condenses with methyl formate in the presence of sodium to give the sodium derivative of methyl α-methoxy-β-hydroxyacrylate, which, after acidification, is reduced (without isolation) by hydrogen and a Raney-nickel catalyst (G.P. 524,086 of 1940) to methyl α-methoxy-β-hydroxypropionate, characterised as its *amide* (V), m. p. 71°. Treated with thionyl chloride and pyridine, this ester affords the corresponding β-chloro-ester, converted by aqueous ammonia into (IV).

The corresponding pair of methoxy-bromopropionamides has also been obtained. Methyl α-bromo-β-methoxypropionate, a specimen of which was kindly supplied by Dr. E. Rothstein of this University, is converted by ammonia into α-*bromo-β-methoxypropionamide* (VI), m. p. 84°. This is isomeric with β-*bromo-α-methoxypropionamide* (VII), m. p. 135°, which was obtained by a reaction sequence similar to that used by Price, Coynes, and De Los de Tar (*J. Amer. Chem. Soc.*, 1941, **63**, 2796) for the synthesis of α-ethoxyacrylonitrile. This paper by the American authors was published just after the corresponding synthesis of *α-methoxyacrylonitrile* (VIII) had been achieved by the present author, using a similar route. β-*Bromo-α-methoxypropionitrile*, obtained in accordance with the scheme: $CH_3{\cdot}CHO + CH_3{\cdot}OH + HCl \longrightarrow CH_3{\cdot}CHCl{\cdot}O{\cdot}CH_3 \xrightarrow{Br_2} CH_2Br{\cdot}CHBr{\cdot}O{\cdot}CH_3 \xrightarrow{CuCN} CH_2Br{\cdot}CH(O{\cdot}CH_3){\cdot}CN$, is converted by dry hydrogen chloride and methyl alcohol in dry ether (cf. Houben and Pfankuch, *Ber.*, 1926, **59**, 2402) into the *imino-ether hydrochloride* (IX), $CH_2Br{\cdot}CH(O{\cdot}CH_3){\cdot}C(O{\cdot}CH_3){:}NH,HCl$, which readily loses methyl chloride when warmed to give the amide (VII). Decomposition of (IX) with ice affords *methyl β-bromo-α-methoxypropionate* (X).

Removal of hydrogen bromide from this ester occurs less readily than it does from the corresponding nitrile. Boiling pyridine, which readily converts the latter into the unsaturated nitrile (VIII), leaves a large proportion of the ester unchanged, but cold piperidine is effective, giving methyl α-methoxyacrylate (XI). This ester was prepared in an impure condition by von Auwers (*Ber.*, 1911, **44**, 3523) by the action of phosphoric oxide on methyl αα-dimethoxypropionate (XII), obtained by condensation of methyl pyruvate with methyl orthoformate, and now characterised as *αα-dimethoxypropionamide* (XIII), m. p. 117°. Prepared by either method, the unsaturated ester is converted by ammonia into *α-methoxyacrylamide* (XIV), m. p. 109°. The same amide results from the elimination of hydrogen bromide from the bromo-methoxyamide (VII) by the action of methyl-alcoholic ammonia. Further confirmation that (VIII) is the α-methoxy-compound accrues from the observation that it is converted, by the action of dry hydrogen chloride and methyl alcohol in dry

* Methyl *d*-αβ-dimethoxypropionate and its amide were prepared by Frankland and Gebhard, J., 1905, **87**, 864.

ether and decomposition of the imino-ether hydrochloride, into (XIII). The orientation of the addition of methyl alcohol thus parallels that of hydrogen bromide to the corresponding α-ethoxyacrylonitrile (Price *et al., loc. cit.*) :



With either addendum the more reactive portion is the positive hydrogen, and the activating polarisation of the ethylenic bond resulting from the $+T$ effect of the α-alkoxy-group predominates over the deactivating polarisation which would result from the electron-attraction of the cyano-group.

α-Methoxyacrylamide also readily adds on one molecule of bromine to give (probably) *αβ-dibromo-α-methoxypropionamide*, m. p. 106°, which is not very stable and, when warmed, readily loses hydrogen bromide.

Experimental.

(All analyses are by Dr. G. Weiler of Oxford.)

Action of Sodium Methoxide on Methyl αβ-Dichloropropionate.—With 2 mols. One half of a solution of 4·6 g. of sodium in 100 c.c. of dry methyl alcohol was added dropwise with mechanical stirring to 15·7 g. of the chloro-ester and 0·1 g. of quinol at 0°. The remaining 50 c.c. was then added, and the mixture stirred at 0° for 2 hours and finally refluxed on a steam-bath for a further hour. After cooling, precipitated sodium chloride (9·5 g.) was removed by filtration, methyl alcohol distilled off through a column, and the product extracted with ether. The highly unsaturated yellow oil (4·5 g.) obtained by evaporation of the washed and dried ethereal solution gave a main fraction, b. p. 140—145°/9 mm., of a colourless, unsaturated, viscous liquid which has not been identified (Found : C, 49·6; H, 6·35%).

With 1 mol. A solution of 2·3 g. of sodium in 50 c.c. of methyl alcohol was similarly added, during 2 hours, to 15·9 g. of the chloro-ester in 50 c.c. of ether at 0°; the mixture was stirred for 1½ hours at 0°, refluxed for ½ hour, kept at room temperature overnight, and worked up as before. Fractional distillation gave *methyl α-chloro-β-methoxypropionate*, b. p. 65·5—66°/11 mm. (Found : C, 40·2; H, 6·4; Cl, 23·8. $C_5H_9O_3Cl$ requires C, 39·4; H, 5·9; Cl, 23·3%). The ester readily dissolved in aqueous ammonia (*d* 0·880) and evaporation of the solution afforded the corresponding *amide* (I), m. p. 61° after crystallisation from ether–ligroin (b. p. 40—60°) (Found : C, 35·3; H, 5·8; N, 10·1. $C_4H_8O_2NCl$ requires C, 34·9; H, 5·8; N, 10·2%).

Action of Sodium Methoxide on Methyl α-Chloro-β-hydroxypropionate.—13·9 G. of this ester were similarly treated with 2·3 g. of sodium in 50 c.c. of dry methyl alcohol. After working up as before, distillation of the residue from the ethereal solution gave, in addition to a large amount of high-boiling residue, a fraction, b. p. 69°/14 mm., converted by aqueous ammonia (*d* 0·880) into the amide (I), m. p. and mixed m. p. 61°.

Methyl β-Hydroxy-α-methoxypropionate.—A mixture of 23·2 g. of methyl methoxyacetate and 14 g. of methyl formate was added dropwise, with constant shaking, to 5·12 g. of " molecular " sodium under a little dry benzene, gently warmed on a steam-bath. An energetic reaction set in and, after 3 hours, the sodium had dissolved. The brown sticky mass of the sodium derivative of methyl β-hydroxy-α-methoxyacrylate was washed by decantation with cold dry ether and dissolved in the minimum quantity of cold water. The aqueous solution, acidified with 105 c.c. of 2N-sulphuric acid, was reduced with hydrogen at 50°/40 atms. and a Raney nickel catalyst. After 6 days (cooling overnight) about 70% of the theoretical volume had been absorbed. The green solution was filtered and concentrated at 30° in a vacuum until oil separated. This was extracted with ethyl acetate and dried over sodium sulphate, and the solvent distilled off through a Widmer column. Fractionation gave 8 g. of methyl β-hydroxy-α-methoxypropionate, b. p. 101—102°/15 mm. (Found : C, 44·5; H, 7·0. Calc. for $C_5H_{10}O_4$: C, 44·8; H, 7·5%), together with a fraction, b. p. 119—127°/16 mm., which gave a purple colour with ferric chloride. The ester was converted by aqueous ammonia into *β-hydroxy-α-methoxypropionamide* (V), m. p. 71° after crystallisation from acetone–ligroin (Found : C, 40·8; H, 7·6; N, 12·0. $C_4H_9O_3N$ requires C, 40·3; H, 7·6; N, 11·8%).

Attempts to dehydrate methyl β-hydroxy-α-methoxypropionate to methyl α-methoxyacrylate with various reagents were unsuccessful, but distillation with phosphoric oxide under atmospheric pressure gave an ester, b. p. 128°/760 mm., which, since it gave a 2 : 4-dinitrophenylhydrazone, seems to be methyl pyruvate, formed by subsequent demethylation and ketonisation of the resulting methyl α-hydroxyacrylate.

β-Chloro-α-methoxypropionamide (IV).—A solution of 2·7 g. of the corresponding hydroxy-ester in 3·5 g. of pyridine was treated with 2·4 g. of thionyl chloride. After initial self-heating, the mixture was warmed on a steam-bath until evolution of sulphur dioxide ceased. The product was extracted with ether and washed successively with saturated brine acidified with dilute hydrochloric acid, and water. Distillation of the residue from the dried ethereal solution gave a small quantity of a chlorine-containing ester, b. p. 88—90°/22 mm., rapidly converted by aqueous ammonia (*d* 0·880) into a crystalline mass of the amide. Recrystallisation from ether or methyl alcohol gave *β-chloro-α-methoxypropionamide* (IV), m. p. 138° (Found : C, 35·3; H, 6·2; N, 9·8. $C_4H_8O_2NCl$ requires C, 34·9; H, 5·9; N, 10·2%).

Action of Sodium Methoxide on αβ-Dibromopropionic Acid.—The acid (23·2 g.) was added to a warm solution of 4·6 g. of sodium in 80 c.c. of dry methyl alcohol. Self-heating occurred and after ½ hour the mixture was nearly solid and neutral. The separated white solid was highly unsaturated and was probably sodium α-bromoacrylate. The mixture was refluxed for 2 hours on a steam-bath and then 0·1 g. of quinol was added, followed by a solution of 2·3 g. of sodium in 50 c.c. of dry methyl alcohol. Refluxing was continued for 20 hours. The methyl alcohol was then distilled off, and the thick pasty mass washed with ether, covered with fresh ether, and just acidified (Congo-red) with dilute sulphuric acid. Rapid distillation of the residue from the washed and dried ethereal solution gave 4·5 g. of a fraction, b. p. 132°/14 mm. A suspension of dry silver oxide in dry methyl alcohol was refluxed with 4 g. of this acid and methyl iodide was added in small successive portions during 40 hours. After evaporation of the methyl alcohol the residue was extracted with dry ether and filtered from silver salts. Evaporation of the ethereal solution caused separation of a small amount of seemingly polymerised material, which was removed. Distillation of the residue gave *methyl αβ-dimethoxypropionate* (II), b. p. 74·5°/14 mm. (Found : C, 48·7; H, 8·0. $C_6H_{12}O_4$ requires C, 48·65; H, 8·1%). With concentrated aqueous ammonia it afforded *αβ-dimethoxypropionamide* (III), m. p. 58° after crystallisation from ether (Found : C, 45·4; H, 8·5; N, 9·9. $C_5H_{11}O_3N$ requires C, 45·1; H, 8·3; N, 10·5%). Methylation of 0·5 g. of methyl

β-hydroxy-α-methoxypropionate by refluxing with 5 c.c. of methyl iodide and dry silver oxide gave a product converted by aqueous ammonia, in small yield, into the same amide, m. p. 53—56°, raised to 55—57° by admixture with (III), m. p. 58°.

β-Bromo-α-methoxypropionitrile and Methyl β-Bromo-α-methoxypropionate.—A mixture of 200 g. of paraldehyde and 220 g. of dry methyl alcohol was cooled in a freezing mixture and saturated with dry hydrogen chloride (250 g.). The top layer (325 g.) of methyl α-chloroethyl ether was dried with calcium chloride and used without further purification. 100 C.c. of dry bromine were added dropwise with constant shaking to 199 g. of the chloro-ether at 0°. After removal of dissolved hydrogen bromide by an air stream, distillation gave a main fraction (372 g.), b. p. 67—75°/21 mm., of methyl αβ-dibromoethyl ether, which was used without further purification. Redistillation gave a purer product, b. p. 67—69°/22 mm. with some loss. A solution of 196 g. of the dibromo-ether in 230 c.c. of sodium-dried ether was added to 90 g. of dry powdered cuprous cyanide in a large flask fitted with an efficient reflux condenser. The mixture was gently warmed, with constant shaking, until a brisk reaction, necessitating ice-cooling, had subsided. The mixture was then refluxed for ¾ hour and kept in the cold for 24 hours to allow separation of copper compounds. Ether from the filtrate and washings of the copper salts was distilled through a Widmer column. The dark coloured residual liquid was decanted from copper compounds which separated during concentration. Fractionation under reduced pressure gave a considerable fraction, b. p. 30—84°/15 mm., and then *β-bromo-α-methoxypropionitrile* (70 g.) was collected at 84—89°/16 mm. The pure nitrile, b. p. 54°/0·1 mm. or 94·5°/24 mm. (Found: C, 29·7; H, 3·9. C_4H_6ONBr requires C, 29·3; H, 3·7%), rapidly decomposed and was immediately converted either into the unsaturated nitrile or into the imino-ether hydrochloride. A mixture of 65 g. of the nitrile, 14 g. of dry methyl alcohol, and 350 c.c. of dry ether was saturated with dry hydrogen chloride at − 10° for 3—4 hours and then kept in a refrigerator for 18 hours. Thorough washing of the separated mass of crystals with dry ether is essential to free the material from volatile halogen-containing products which are difficult to remove at later stages. The *imino-ether hydrochloride* (IX) thus obtained was almost pure (Found: C, 25·3; H, 5·3; Cl, 16·4. $C_5H_{11}O_2NClBr$ requires C, 25·8; H, 4·8; Cl, 15·3%). The chloride ion analysis was carried out on an earlier sample which may have retained traces of free hydrogen chloride.

The imino-ether hydrochloride, stirred under ether at 0°, was decomposed by gradual addition of melting ice. After complete solution had occurred, the stirring was continued at 0° for about 20 minutes to complete the decomposition (otherwise the product is contaminated with the amide) and the aqueous layer was extracted several times with ether. After removal of the solvent from the washed and dried extract through a Widmer column, fractionation of the residue gave 45 g. of *methyl β-bromo-α-methoxypropionate* (X), b. p. 49°/0·5 mm. (Found: C, 31·3; H, 4·8; Br, 40·2. $C_5H_9O_3Br$ requires C, 30·5; H, 4·6; Br, 40·6%).

The imino-ether hydrochloride readily decomposes on warming either alone or in aqueous solution to give *β-bromo-α-methoxypropionamide* (VII), m. p. 135° after crystallisation from water (Found: C, 26·6; H, 4·5; N, 7·9; Br, 44·0. $C_4H_8O_2NBr$ requires C, 26·4; H, 4·4; N, 7·7; Br, 44·0%). This amide is isomeric with *α-bromo-β-methoxypropionamide* (VI), m. p. 84° after crystallisation from ether (Found: C, 26·6; H, 4·4%), which was prepared from a specimen of methyl α-bromo-β-methoxypropionate kindly supplied by Dr. Rothstein of this University.

α-Methoxyacrylonitrile (VIII).—Freshly distilled β-bromo-α-methoxypropionitrile (54 g.) was added dropwise to 50 g. of boiling pyridine (dried over potassium hydroxide and distilled) under reflux, and boiling continued for 10 minutes thereafter. If the reactants are pure and dry, pyridine hydrobromide separates as a white crystalline mass from a red solution. After cooling, the pyridine hydrobromide was repeatedly extracted with boiling ether and the extracts were washed free from pyridine with 2N-hydrochloric acid and water. The ether was removed from the dried solution through a Widmer column, and the residue distilled. *α-Methoxyacrylonitrile* (VIII), b. p. 27·5°/15 mm. or 32·5°/23 mm., was obtained as a colourless mobile liquid (Found: C, 57·8; H, 6·5; N, 17·0. C_4H_5ON requires C, 57·8; H, 6·1; N, 16·9%).

A solution of 1 c.c. of the unsaturated nitrile in 5 c.c. of dry ether and a few drops of dry methyl alcohol was saturated at 0° with dry hydrogen chloride. The solution (containing some crystalline material) was evaporated in a current of dry air under reduced pressure, and the yellow viscous mass extracted with warm dry ether. The residue from the ethereal solution crystallised after seeding. Crystallisation of the product from ether gave a saturated amide, m. p. 113°, depressed by admixture with α-methoxyacrylamide, m. p. 109°, but raised to 116° by admixture with αα-dimethoxypropionamide, m. p. 116° (below).

Methyl α-Methoxyacrylate (XI).—A solution of 18 g. of redistilled piperidine in its own volume of dry ether was added dropwise to a solution of 39 g. of methyl β-bromo-α-methoxypropionate and 0·1 g. of quinol in 50 c.c. of dry ether at 0°, more ether being added as the mixture became thick with separated piperidine hydrobromide. After keeping at room temperature for 18 hours, the piperidine hydrobromide was removed by filtration. The residue from the ethereal solution, freed from piperidine and solvent as above, was distilled. Methyl α-methoxyacrylate (18 g.), b. p. 51·5—52°/11 mm., was obtained (Found: C, 50·9; H, 7·2; OMe, 51·3.* Calc. for $C_5H_8O_3$: C, 51·7; H, 6·9; OMe, 53·4%). The ester was converted by ammonia into the same amide, m. p. and mixed m. p. 109°, as that prepared from the specimen of ester obtained from methyl αα-dimethoxypropionate (XII). The latter ester, b. p. 59·5°/11 mm. (Found: C, 48·6; H, 8·6. Calc. for $C_6H_{12}O_4$: C, 48·6; H, 8·2%), was obtained by the condensation of 18 g. of methyl pyruvate with 25 g. of methyl orthoformate in 90 c.c. of dry methyl alcohol containing 1 g. of ammonium chloride (von Auwers, *loc. cit.*). It was converted by aqueous ammonia into its *amide* (XIII), m. p. 117° after crystallisation from ether (Found: C, 45·8; H, 8·3; N, 10·95. $C_5H_{11}O_3N$ requires C, 45·1; H, 8·3; N, 10·5%). The unsaturated ester obtained by the action of phosphoric oxide on methyl αα-dimethoxypropionate by von Auwers's method had b. p. 55·5°/10 mm., but, in agreement with the findings of that author, did not seem to be quite pure (Found: C, 50·5; H, 8·0; OMe, 56·2.* Calc. for $C_5H_8O_3$: C, 51·7; H, 6·9; OMe, 53·4%). It was probably contaminated with a little of the unchanged dimethoxy-ester. It was, however, characterised as *α-methoxyacrylamide* (XIV), m. p. 109° after crystallisation from ether (Found: C, 47·6; H, 7·3; N, 14·1. $C_4H_7O_2N$ requires C, 47·5; H, 6·9; N, 13·9%). Ozonolysis of the unsaturated ester afforded formaldehyde, identified as its dimedon compound, m. p. and mixed m. p. 189°, but methyl oxalate could not be isolated as such. From its hydrolysis product, however, oxalic acid dihydrate, m. p. and mixed m. p. 100°, was isolated and exhibited its characteristic properties.

α-Methoxyacrylamide (0·3 g.) was treated with 0·5 g. of dry bromine, both in solution in dry carbon tetrachloride, until just coloured and the solution was evaporated to dryness on a steam-bath. The product was dissolved in dry ether and concentrated, and light petroleum (b. p. 40—60°) added. The *αβ-dibromo-α-methoxypropionamide* obtained had m. p. 106° after crystallisation from benzene–light petroleum (b. p. 60—80°). It readily lost hydrogen bromide in the air and was not quite pure (Found: Br, 60·2. $C_4H_7O_2NBr_2$ requires Br, 61·3%).

The author is indebted to Messrs. I.C.I. (Dyestuffs), Ltd., for a grant, for gifts of chemicals, and for permission to publish this investigation.

THE UNIVERSITY, LEEDS. [*Received, April 23rd*, 1942.]

* Unreliable values for methoxyl were obtained with all the compounds examined in this investigation, even when the purity of the compound was proved by the figures for carbon and hydrogen.

98. *Rare-earth Metal Amalgams. Part II. The Separation of Neodymium, Samarium, and Gadolinium.*

By Joseph K. Marsh.

By treating neodymium–samarium or samarium–gadolinium acetates with sodium amalgam, samarium, which readily forms an amalgam, is at once separated. Fractional decomposition of the samarium amalgam gives further purification, for this amalgam is much less stable than those of neodymium and gadolinium. In one operation the neodymium content in samarium is reduced from 70% to 0·01%.

It was shown in Part I (this vol., p. 398) that by reaction between sodium amalgam and rare-earth acetates widely differing amounts of rare-earth metal amalgams were formed. In the case of samarium practically quantitative transfer from aqueous acetate solution to mercury was brought about. This reaction has now been studied more fully and applied as a method for rare-earth purification. The separation of neodymium–samarium or samarium–gadolinium mixtures has been achieved with greater ease and completeness than by any of the known methods, but europium if present accompanies samarium in the separation. McCoy (*J. Amer. Chem. Soc.*, **1935**, **57**, 1756; **1937**, **59**, 1131; **1941**, **63**, 3422) has, however, described three easy ways of separating these two elements, the latest of which makes use of the preferential amalgam formation by europium on electrolysis. Only small amounts of europium oxide were present in any of the earths used in the present investigation, so for the purposes of this communication europium and samarium may be regarded as a single element.

The conditions most applicable to the extraction of samarium by amalgam formation from neighbouring elements other than europium depend upon their relative amounts. If samarium greatly preponderates in a rare-earth mixture, it may be separated as amalgam from a slightly alkaline acetate solution by the use of sodium amalgam, the efficiency for the sodium–samarium exchange $3Na + Sm^{\cdots} = 3Na^{\cdot} + Sm$ being 90%. A p_H of 8—9 is favourable, *i.e.*, the solution should be almost at the point of hydroxide precipitation. When samarium is only present in small amount, however, it is best to carry out the reaction under conditions suited to give maximum production of amalgam of the element forming the main constituent of the rare-earth mixture. If this element is neodymium or gadolinium, a p_H of 4—5 is suitable. Care should be taken that about 10% of the sodium in the amalgam is left when the reaction is stopped; otherwise, some of the samarium may pass back from amalgam to solution at the end. It is impossible therefore to lay down precise conditions for treating rare-earth mixtures the composition of which will often be known only approximately. The reducing action may take only 1—5 minutes and cannot be brought under accurate control.

Separation of the rare-earth elements occurs both on amalgam formation and on amalgam decomposition. Samarium forms amalgam much more readily than neodymium or gadolinium, but the amalgam is less stable and by attack with water or dilute acid will react almost completely before there is any considerable decomposition of the other constituent. By this two-fold reaction neodymium has been reduced from 70% to 0·01% in a samarium preparation, and in two extractions about 80% of the samarium handled had the neodymium removed to this limit. In the case of gadolinium in samarium it is not possible to estimate traces with the same facility as traces of neodymium owing to the lack of suitable strong absorption bands, but the following considerations show that the separation is likely to be at least as good. The maximum yields of oxides from amalgam per g. of sodium which have been obtained are: Nd, 0·18; Gd, 0·018 g. Optimum conditions are similar in the two cases, but the yield of neodymium is ten times as great as that of gadolinium. No change in proportion of the two earths was, however, observable when their mixed amalgam was fractionally decomposed. Gadolinium and neodymium are therefore about equally stable in amalgam, but gadolinium forms less amalgam in the first instance. There is therefore every reason to think that the separation of samarium and gadolinium by amalgam formation is at least as efficient as that of neodymium and samarium.

The amount of residual samarium left in neodymium or gadolinium is also not easy to estimate, for the visible absorption bands are not sensitive, and observation of the band at 10869 A. is beyond ordinary resources. It was found that, while at first samarium could easily be separated from neodymium or gadolinium, yet soon the yield fell to almost zero. The amount remaining was not detectable by arc or absorption spectroscopy. In the case of gadolinium by 6 successive similar treatments with sodium the yield of samarium oxide recovered fell from 6 g. to 1 mg. (Table I), leaving 48 g. of purified oxide. There is no reason to suppose that more than a fraction of a mg. (or, say, 0·001%) of samarium remained with the gadolinium.

After a few treatments of a rare-earth acetate solution with sodium, the efficiency of the extraction falls off in accordance with the law of mass action. The accumulated sodium acetate also tends to salt out samarium or gadolinium acetate, and it is easy to recover 90% of them free from sodium acetate by crystallisation. Neodymium, on the other hand, gives a stable acetate tetrahydrate only at room temperature, and on warming, a less soluble salt is precipitated. Neodymium solutions must therefore be used cold. The separation from sodium is also less satisfactory.

Experimental.

Materials.—All the rare-earth materials had been fractionated as double magnesium nitrates, and the europium removed from the samarium–gadolinium intermediates by McCoy's method with a Jones reductor. Only small amounts of europium remained in any of the material used. The neodymium–samarium mixture was the head fractions from a

samarium fractionation; it gave a brown oxide due to the presence of a little praseodymium but the spectrum showed only a trace of lanthanum.

Sodium amalgam was made by direct union and stored as a crystalline solid of about 2% strength. It was dissolved in mercury just before use to 0·25—0·33% concentration—the exact value should be known in order to gauge the equivalent amount of acetic acid.

The acetates were prepared as crystalline salts before use. Gadolinium and samarium are known to give tetrahydrates, but neodymium gives several hydrates and difficulty was experienced through the precipitation of a salt of lower solubility when a concentrated, cold acetate solution was heated.

Quantitative estimates of components of rare-earth mixtures have where possible been made by comparison of absorption spectra of solutions with standards.

Separation of Samarium and Gadolinium.—The mixed oxides (65 g.) of gadolinium (89%) and samarium (11%) were converted into acetate (143 g.), dissolved in 325 ml. of boiling water, and treated hot with sodium (7·5 g.) in mercury (175 ml.). During the reaction, which took only a few minutes, 12 ml. of glacial acetic acid were added. The reaction mixture was shaken gently in a 1-l. flask and then separated in a tap funnel. There was still some sodium remaining in the mercury. The samarium absorption spectrum at the conclusion indicated roughly 5 g./l. of oxide in solution.

The washed amalgam was shaken with water till the sodium was removed. It was then treated with 2N-hydrochloric acid and shaken till calomel began to form. The acid extract was treated with oxalic acid, and the resulting oxalate ignited, affording 6·1 g. of samaria. The above procedure was repeated after adding 300 ml. of water to the acetate solution; 20 ml. of acetic acid were used this time, and the solution finally had p_H 6 (B.D.H. universal indicator). No absorption spectrum was now detectable; yield of samaria, 0·89 g. A third extraction with sodium amalgam (6·4 g. Na) gave a further yield of 0·14 g. of oxide. The oxalate of this material was too pale to be that of pure samarium. The acetate solution was now concentrated to 300 ml. and set aside to crystallise; yield, 122 g. of rare-earth acetate. The mother-liquor containing all the sodium acetate was treated with sodium hydroxide, and gadolinium oxide (4·2 g.) recovered from it. This was not worked further. Frequent sodium acetate removal is desirable, as shown by an increased amalgam yield in the following extraction.

In the fourth extraction gadolinium acetate (122 g.), water (300 ml.), sodium (6·4 g.) in mercury (175 ml.), and acetic acid (20 ml.) were used. Only a little sodium remained in the mercury when it was separated from the acetates. The mercury was shaken with water. At first the sodium reacted, then the mercury broke into droplets and formed a mud. At this stage hydroxide precipitate began to appear in the water. After being shaken for a short time the sludge broke down and the mercury coalesced once more. The hydroxide which had now formed was collected. The mercury was again shaken with water; more hydroxide was formed, but no sludge. The mercury was finally shaken with hydrochloric acid till calomel formation started. It was found that the hydroxide (75 mg. of oxide) formed during the mercury sludge period gave a yellow oxalate and chloride solution, and strong samarium absorption spectrum, whereas the rare-earth oxide recovered subsequently gave a white oxalate and no absorption spectrum in chloride solution. The spectrum would have revealed 0·6% of samarium. Arc spectroscopy gave confirmatory results. The first crop hydroxide was found to have been samarium with a little europium and gadolinium, but the second crop was pure gadolinium.

In the fifth extraction 100 ml. more of water were used, but only 10 ml. of acetic acid. There was thus considerable sodium left in the amalgam when it was separated from the acetates. This gave greater protection to the samarium in the amalgam, for sodium suffers attack and removal almost quantitatively before any rare earth. The sodium was laboriously removed from the mercury by shaking with several changes of water, but eventually only a very little mercury sludge formation occurred. The hydroxide precipitate at this stage was too small to handle, so acid was added, and the total rare-earth extracted from the amalgam (62 mg. of oxide). The absorption spectrum of this oxide, examined as chloride, led to an estimate of a content of 10 mg. of samaria.

At this point the gadolinium acetate was again purified from sodium acetate and 5·1 g. of gadolinium oxide rejected. The sixth extraction was given in 250 ml. of hot gadolinium acetate solution. The rare earth obtained from the amalgam afforded 120 mg. of oxide. This was converted into chloride, and the absorption spectrum examined in 0·22 ml. (l = 6 cm.). The presence of 1 mg. of samarium oxide should have been detectable, and just about this amount appeared to be present. The foregoing results are summarised in Table I.

TABLE I.

The separation of samarium and gadolinium by extraction with sodium amalgam.

Extraction no.	1.	2.	3.	4.	5.	6.
Na used, g.	7·5	6·4	6·4	6·4	6·4	6·4
Acetic acid, ml.	12	20	20	20	10	17
Yield of Sm_2O_3, g.	6·1	0·9	0·14	0·075	0·010	0·001
Yield of Gd_2O_3, g.				0·090	0·052	0·120
Residue, Gd_2O_3, g.			4·2		5·1	48

Purification of Gadolinium.—This was effected in a similar manner to the later extractions of the samarium–gadolinium mixture (above), but the impurity was chiefly europium. Gadolinium acetate (140 g.) was treated in 250 ml. of boiling water with 6·4 g. of sodium in 175 ml. of mercury, and during the reaction 17 ml. of acetic acid were added. A little sodium remaining in the amalgam at the end of the reaction was removed by shaking with water. The mercury then formed a sludge. The hydroxide which had formed when the sludge broke down again yielded 141 mg. of oxide showing the green reflection bands of europium distinctly but not so strongly as pure europium oxide. The arc spectrum confirmed the presence of some gadolinium. Oxide (40 mg.) recovered from amalgam subsequent to sludge formation showed no reflection bands or absorption spectrum in 1 cm. of 200 g./l. of oxide in solution as chloride. The europium oxide content was therefore under 1·25%.

130 G. of gadolinium acetate crystallised out from the solution on cooling. It was given a second extraction with 6·4 g. of sodium as above. The oxide (85 mg.) recovered from amalgam gave no europium reflection or absorption spectrum. The main bulk of gadolinium was now found to be free from any trace of europium arc lines.

Purification of Samarium.—The sample of oxide used had been fully fractionated as double magnesium nitrate but came from the more soluble end of the samarium fractions. It might therefore contain a little europium or gadolinium.

Samarium acetate (80 g. = 35 g. of oxide), boiling water (200 ml.), and sodium (5·4 g. in 175 ml. of mercury) were shaken together gently till a dark red colour developed (1 min.), and the amalgam was then separated. It was slightly pasty and contained no sodium. Solid samarium amalgams result, and are troublesome to separate, if sodium amalgam exceeding 0·25% concentration is used to extract samarium from solutions where a high yield is to be expected. The solubility of samarium in mercury cannot be above 0·5%.

The foregoing reaction was repeated with the addition of 0·6 ml. of acetic acid at the start and 1 ml. during the course of the reaction (4 mins.). The solution was frothy all the time, indicating an alkaline state. Escaping hydrogen was not noticeable. The resulting samarium amalgam was a little pasty and the mercury showed a tendency to emulsify and form black clots with samarium hydroxide. The separated amalgam was treated with insufficient concentrated hydrochloric acid, and the strong, dark red colour of samarous salts developed as the solution became alkaline. Some of the red-brown solution was decanted and kept in a beaker. At first there was a rapid evolution of hydrogen and a green precipitate formed, but some colour persisted for more than an hour. The amalgam was extracted with more hydrochloric acid.

In making a third extraction of the acetate solution, only half the previous amount of sodium amalgam was used. Acetic acid (1·5 ml.) was added at the beginning. The whole of the sodium reacted in 2 mins. A fourth extraction similar to the third but without the addition of more acetic acid was made. The solution was frothy and much sodium remained. Rare earth (2·4 g. of oxide) still in solution as acetate was recovered as hydroxide and reconverted into acetate. This was then extracted four times with 0·4 g. of sodium in 25 ml. of mercury each time. The residue subsequently recovered as hydroxide gave a pale brown oxide and showed no samarium reflection bands. These separations are summarised in Table II.

TABLE II.

Purification of samarium by amalgam formation.

Extraction no.	1.	2.	3.	4.	5.	6.	7.	8.	Total.
Na used, g.	5·4	5·4	2·7	2·7	0·4	0·4	0·4	0·4	
Acetic acid, ml.	0	1·6	1·5	0	0	0·7	0	1	
Yield of Sm_2O_3, g.	12·0	12·9	4·7	1·4	0·75	1·11		0·15	33·0
Residue unamalgamated ...	0·1 g.	Washings, etc., 1·9 g.							

In this purification no attempt was made to separate samarium and gadolinium on decomposition of the amalgams. A very slight trace of gadolinium was found by arc spectroscopy in the samarium from the first extraction; the third and the fifth extraction showed small but increasing quantities. The residue was largely but not entirely gadolinium. The work was done before the importance of the fractional decomposition of the amalgams was realised, but it was shown later that the separation of samarium and gadolinium should be equally as good as the separation of samarium and neodymium.

Separation of Neodymium and Samarium.—The acetate used was derived at an early stage from the heads of a fractional crystallisation series of samarium magnesium nitrate. Besides neodymium it contained enough praseodymium to cause the derived oxide to be brown. Lanthanum was also detectable. The neodymium acetate prepared by evaporation at 30° of the solution of the oxide in acetic acid appeared similar in crystalline form to samarium acetate tetrahydrate, but was more soluble. On being heated, a concentrated solution would usually deposit a less soluble salt. The nearly boiling solutions used in other instances were therefore unsuitable. The acetate (120 g. = 50 g. of oxide) was dissolved in 300 ml. of cold water, and sodium (6·4 g.) in mercury (200 ml.) added, and in the course of the reaction 12 ml. of acetic acid. The reaction mixture was shaken gently in a 1-l. flask as before. The mercury was separated and washed twice with water and then shaken in a tap funnel with 2N-hydrochloric acid. The sodium was found to be exhausted. When with excess acid present the evolution of hydrogen slackened the acid was separated with its rare-earth content (Table III, Extraction 1, Crop 1). More acid was shaken with the mercury; extraction then appeared to be almost complete (Crop 2). The mercury was now shaken with water. Hydroxide formed but not a mercury sludge, so the water was acidified and withdrawn (Crop 3). The mercury was finally shaken with acid till calomel formation began (Crop 4).

The acetates were given a repetition of the previous extraction. The reaction was vigorous, but the mixture frothed towards the end. The mercury on withdrawal still held sodium. It was twice washed and then treated with 2N-hydrochloric acid till sodium was removed. On addition of alkali to the sodium solution, a little rare earth was found (Table III, Extraction 2, Crop 1). The amalgam was then treated with 2N-acid till extraction of samarium appeared complete (Crop 2). By shaking the mercury and water some hydroxide was formed (Crop 3). A final treatment of the mercury with acid gave a pale neodymium-coloured solution (Crop 4). A third extraction of the acetate solution was made on similar lines. Most of the crops were made into chloride solutions and the neodymium content estimated from the absorption spectrum, giving the results recorded in Table III.

TABLE III.

Separation of neodymium and samarium by sodium amalgam.

	Extraction 1.				Extraction 2.		Extraction 3.	
	Oxide, g.	Oxide colour.	Nd_2O_3, %.	Nd_2O_3, g.	Oxide, g.		Oxide, g.	
Crop 1	8·07	Sm_2O_3	0·01	0·001	0·035		0·042	
Crop 2	1·04	Sm_2O_3	0·04	0·0004	3·52	0·01% Nd_2O_3	0·60	4% Nd_2O_3
Crop 3	0·140	Buff	1·2	0·0017	0·36	Buff	0·16	Brown
Crop 4	0·144	Brown	50	0·072	0·24	Brown	—	
	9·4			0·075	4·155		0·80	

As the earth mixture was not in the first place binary, further separation would not have resulted in any pure neodymium; 1—2% of samarium was probably still present in the neodymium, but neodymium and sodium acetates do not separate with the same ease as gadolinium and sodium acetates by crystallisation from solution. For further treatment, precipitation of the neodymium as oxalate and reconstitution of the acetate would have been necessary. The recovery of pure samarium has however been most satisfactory, and further recovery would not be economic.

Relative Stability of Neodymium and Gadolinium Amalgams.—Gadolinium acetate (8 g.) and neodymium acetate (0·8 g.), dissolved in hot water (25 ml.) and treated with sodium (0·5 g.) in mercury (7 ml.) with addition of acetic acid (1·4 ml.), gave an amalgam. This might be expected to contain approximately equal quantities of neodymium, and gadolinium, the quantities of acetates mixed being inversely proportional to the amalgam-forming powers.

The amalgam was decomposed in four fractions, the first by water and the other three by 2N-hydrochloric acid. The

four oxides were recovered and examined by arc spectroscopy. No difference in the relative amounts of the two earths in the first and the fourth fraction could be detected, but the first contained traces of europium. The four oxalates were similar in tint.

The amalgams of neodymium and gadolinium are therefore of similar stability, but as gadolinium forms amalgam less readily than neodymium the purification of samarium from gadolinium should be even more satisfactory than the separation from neodymium described above.

Purification of Neodymium.—The material had been subjected to 2000 crystallisations as double magnesium nitrate and came from a fraction near the tail of the neodymium salt and so might contain traces of samarium.

Neodymium acetate (65 g.) was dissolved in water (250 ml.) and treated with sodium (4 g.) in mercury (50 ml.) and acetic acid (11 ml.), reaction being vigorous; after being washed, the mercury was treated with 2N-hydrochloric acid, which reacted with the sodium amalgam present, and a little neodymium was also extracted. The rare earth was precipitated from the acid as hydroxide (giving 10 mg. of oxide). The arc spectrum showed it to be largely neodymium but to contain also considerable samarium. The mercury was then treated with concentrated hydrochloric acid and yielded 0·71 g. of neodymia. A second extraction yielded 0·014 g. of oxide as a first crop and 0·575 g. as a main crop. The two crops gave identical spectra; no samarium was detectable in either. All the samarium present in the specimen of neodymium had therefore been removed by the first extraction with sodium. This result would not be obtained, however, if there was not considerable sodium left in the amalgam when the reaction was stopped, for then samarium might pass back from amalgam to solution.

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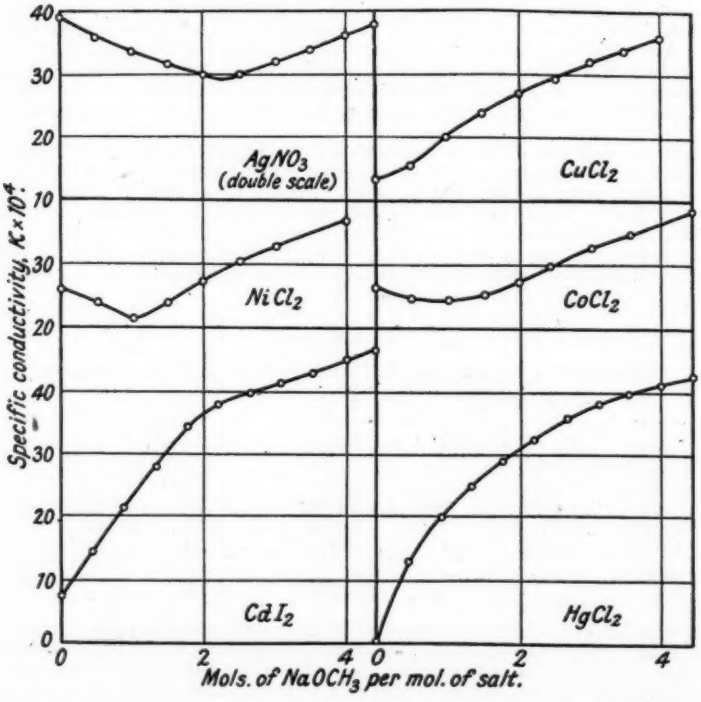
99. *Studies of Ionisation in Non-aqueous Solvents. Part V. The Formation of Certain Methoxides and Ethoxides in Methyl and in Ethyl Alcohol.*

By WILLIAM L. GERMAN and THOMAS W. BRANDON.

The reactions between solutions of sodium methoxide and of sodium ethoxide and conveniently soluble salts in methyl and ethyl alcohols have been studied with the aid of conductivity titrations. As with dilute solutions of sodium hydroxide in water, the reactions, in most cases, lead to the formation of basic compounds.

THE reactions between certain metallic salts and (i) sodium methoxide in methyl alcohol and (ii) sodium ethoxide in ethyl alcohol have been studied with the aid of conductivity titrations. Britton (J., 1925, **127**, 2110) has shown that aqueous sodium hydroxide precipitates basic salts from dilute solutions of most of the

FIG. 1.



salts here discussed, and it appears that similar results are obtained when sodium hydroxide is replaced by sodium methoxide or ethoxide, and the solvent medium by methyl or ethyl alcohol. This similarity is not surprising in view of the high degree of ionisation of these salts in the two alcohols, as the following table shows.

Values of Λ/Λ_∞ *at* 18°.

$c \times 10^4$.	19·5.	39.	78.	156.	Ref.
NaOH in water	0·98	0·97	0·96	0·93	I.C.T., Vol. VI.
$NaOCH_3$ in $CH_3{\cdot}OH$	0·86	0·82	0·77	0·73	Tijmstra, *Z. physikal. Chem.*, 1904, **49**, 350.
$NaOC_2H_5$ in $C_2H_5{\cdot}OH$	0·83	0·76	0·66	0·60	Hengevelt, Thèse, 1911.

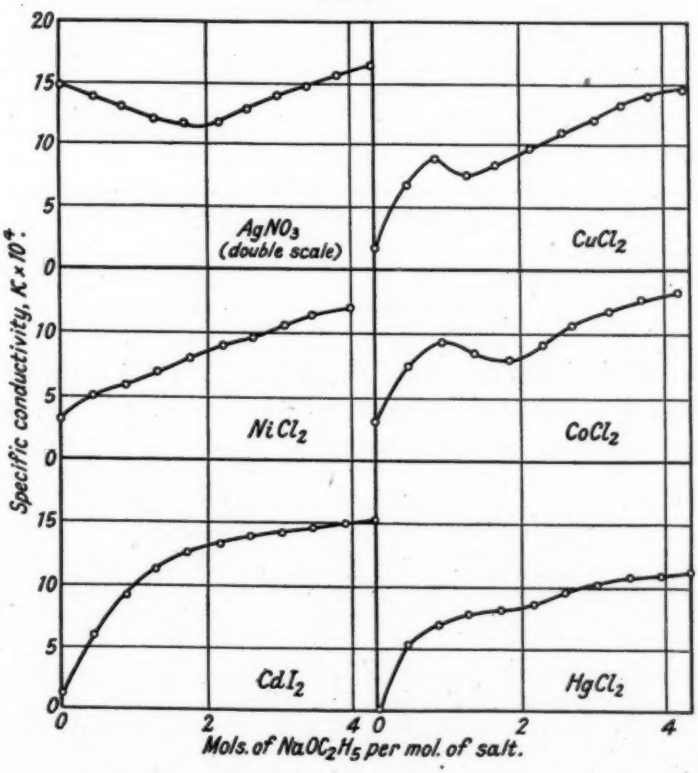
Experimental.

The solutions of sodium alkoxide were prepared by dropping clean, dry sodium into the alcohol, purified as described in Part I (J., 1938, 1027), moisture being excluded. They were analysed by diluting a sample with water and titrating it with standard hydrochloric acid. The stock solution was then diluted with the alcohol until approximately 0·1N.

The conductivity apparatus was the same as already described (Part I, *loc. cit.*). The compounds for analysis were prepared by mixing the appropriate solutions and allowing them to stand. The precipitates were filtered off in a dry atmosphere, well washed with the dry alcohol, and then placed in a vacuum desiccator over fused calcium chloride and evacuated at intervals until constant weight was obtained. The precipitates were then dissolved in excess of standard dilute acid and the OR radical determined by titrating the excess acid with standard sodium hydroxide solution: $XOR + HCl = XCl + HOR$ (X = univalent metallic radical; R = alkyl group). The metallic contents of the precipitates were determined by the usual methods.

The results of the conductivity titrations in methyl and in ethyl alcohol are given in Figs. 1 and 2 respectively.

Fig. 2.



Reactions with Silver Nitrate.—With both sodium methoxide in methanol and sodium ethoxide in ethanol, brownish-black precipitates were formed in which the ratio of metal to alkyl radical was 1 : 1. The conductivity curves show a decided break in each case at this point, and the reaction is thus one of complete double decomposition: $AgNO_3 + NaOR = AgOR\downarrow + NaNO_3$.

Reactions with Cadmium Iodide.—With sodium methoxide instantaneous double decomposition took place, with deposition of a white *precipitate* (Found: Cd, 53; OMe, 29%. Cd : OMe = 1 : 1·98) which settled readily. The conductivity curve changes direction after the addition of two molecules of methoxide and the reaction is thus one of simple double decomposition.

With sodium ethoxide in ethanol no immediate precipitation occurred, and only after the addition of rather less than 2 mols. did a white, gelatinous precipitate begin to form. The conductivity titration indicates that this substance was of indefinite composition, but on standing in contact with excess ethoxide it changed into a normal *compound* (Found: Cd, 53·2; OEt, 42·6%. Cd : OEt = 1 : 2·01).

Reactions with Copper Chloride.—With both alkoxides indefinite compounds were formed. With sodium methoxide precipitation was delayed until about 1 mol. of methoxide had been added, the first precipitate being light green and gelatinous. After 2 mols. had been added the precipitate was emerald-green, becoming blue and voluminous, but the conductivity curve shows that reaction was complete before this stage. The precipitate was therefore basic, and one prepared by adding excess of sodium methoxide to copper chloride solution had the composition: Cu, 51·9; OMe, 40·4%. Cu : OMe = 1 : 1·60.

With sodium ethoxide in ethanol the reaction was similar, precipitation being slow at first, and the initial light

green precipitate turned black when excess of the ethoxide had been added. This precipitate was a basic compound (Found: Cu, 39·3; OEt, 50·1%. Cu : OEt = 1 : 1·80). The conductivity curve indicates that the reaction does not afford a definite compound.

Reactions with Cobalt Chloride.—When sodium methoxide solution was added to a solution of cobalt chloride in methanol there was no immediate precipitation but the solution became turbid and further additions led to deposition of a white flocculent precipitate, which gradually changed to a dirty buff colour, leaving a colourless supernatant liquid. The conductivity curve indicates that the reaction is complete before 2 mols. of methoxide have been added, and that the precipitate is of indefinite composition. One prepared by adding excess of methoxide solution to the cobalt chloride solution had the composition: Co, 43·5; OMe, 41·1%. Co : OMe = 1 : 1·94. In ethanol, sodium ethoxide showed a similar behaviour: a white gelatinous precipitate formed slowly, which gradually darkened, and when 1 mol. of the ethoxide solution had been added the solution was practically colourless. The conductivity curve shows an inflexion after the addition of between 1 and 2 mols. of ethoxide, indicating formation of a basic substance. When excess of the ethoxide was present the precipitate had turned brown and settled readily (Found: Co, 41·9; OEt, 46·3%. Co : OEt = 1 : 1·57).

Reactions with Nickel Chloride.—Addition of sodium methoxide caused no precipitation until rather more than 2 mols. had been added, whereupon there was a slight turbidity. The conductivity curve showed a break when rather less than 1 mol. had been added, indicating basic compound formation. This is confirmed by analysis of the whitish-green precipitate formed by adding excess of methoxide to the nickel chloride solution and allowing it to stand (Found: Ni, 41·1; OMe, 33·5%. Ni : OMe = 1 : 1·54).

In the reaction with sodium ethoxide the conductivity curve gave no indication of definite compound formation; precipitation was obtained more readily than in the previous case, the precipitate being light green and flocculent. That obtained by adding excess of sodium ethoxide to the nickel chloride solution was of indefinite composition (Found: Ni, 40; OEt, 55·9%. Ni : OEt = 1 : 1·82).

Reactions with Mercuric Chloride.—Solutions of mercuric chloride gave an intense orange precipitate when solutions of sodium methoxide in methanol were added. The conductivity curve changed direction after the addition of rather less than 1 mol. and the precipitate was basic. The compound prepared by adding excess of the methoxide was insoluble in dilute acid, and only the metal was determined [Found: Hg, 85·4. Calc. for $Hg(OMe)_2$: Hg, 76·5%].

In ethanol, sodium ethoxide precipitates from mercuric chloride an orange precipitate. The conductivity curve shows a discontinuity after the addition of 2 mols., indicating formation of a definite *compound* [Found: Hg, 68·7. $Hg(OC_2H_5)_2$ requires Hg, 69·0%].

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100. *A Potentiometric Study of the Oxidation of Phenylhydrazine by Cupric Ions, including the Titration of Fehling's Solution with Phenylhydrazine.*

By H. T. S. BRITTON and E. MAY CLISSOLD.

The oxidation of phenylhydrazine by cupric ions present in complex solutions, *viz.*, as tartrate, together with caustic alkali, borax, or alkali phosphate, acetate, or carbonate, has been investigated potentiometrically at 93°. Benzene and phenol are formed simultaneously, and the results show that, when the difference between the potentials set up at a platinum electrode before and after the completion of the oxidation is small, the amount of benzene formed predominates, but when the difference is large a greater proportion of phenol is produced. Under carefully controlled conditions in regard to the reactants, the potentiometric method is particularly suitable for the quantitative estimation of phenylhydrazine with an accuracy greater than that of the usual gasometric nitrogen method.

BRITTON and KÖNIGSTEIN (J., 1940, 673) have shown that hydrazine and hydroxylamine may be potentiometrically estimated by means of Fehling's solution at 90°. The present work is an extension of this method to the estimation of phenylhydrazine. Unlike that of hydrazine and hydroxylamine, however, the oxidation of phenylhydrazine cannot be expressed by a definite stoicheiometric equation, and this militates against the titration as a quantitative method, but if precautions are taken with regard to (*a*) temperature and (*b*) concentrations of the reactants, the method is capable of yielding results that are more accurate than those obtained by the usual method in which the volume of nitrogen evolved is measured (Strache, see Smith, *Chem. News*, 1906, **93**, 83; Thorpe and Whiteley, "Organic Chemical Analysis," London, 1925, p. 182; Ellis, J., 1927, 848; Marks and Morrell, *Analyst*, 1931, **56**, 512).

Phenylhydrazine on oxidation with Fehling's solution yields benzene and phenol in approximately equimolecular ratio. At room temperature the reaction is slow, requiring ½ hour for completion (Maclean, *Biochem. J.*, 1913, **7**, 511; Marks and Morrell, *loc. cit.*), whereas at 93° the present work shows that it is almost instantaneous. The equation usually assigned to the reaction is

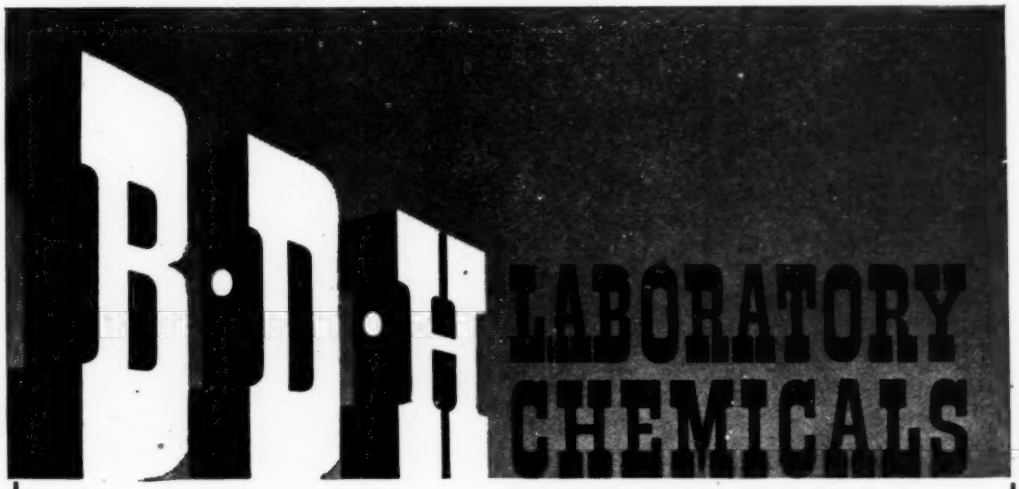
$$2C_6H_5\cdot NH\cdot NH_2 + 6CuO \longrightarrow C_6H_6 + C_6H_5\cdot OH + 2N_2 + 2H_2O + 3Cu_2O$$

but calculation from Maclean's data shows that benzene and phenol were produced at room temperature in the ratio of 17 : 83, whereas Marks and Morrell's data reveal variations in this ratio between 37·5 : 63·5 and 48·5 : 51·5. It is clear, therefore, that the oxidation process consists of two separate reactions, *viz.*,

$$C_6H_5\cdot NH\cdot NH_2 + 2CuO \longrightarrow C_6H_6 + N_2 + H_2O + Cu_2O$$

and

$$C_6H_5\cdot NH\cdot NH_2 + 4CuO \longrightarrow C_6H_5\cdot OH + N_2 + H_2O + 2Cu_2O$$



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